DEVELOPMENT OF A MODEL TO BE USED AS AN INDICATOR OF OILY WASTEWATER POLLUTION, FINGERPRINTING AND COMPLIANCE USING DIMENSIONAL ANALYSIS

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by

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I, with this dissertation declare that it is my own work and that all the quoted and used sources have been shown and recognised by means of complete references.

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DEDICATION

This dissertation is dedicated to my two beautiful daughters, Kutloano Monatisa and Bonang Monatisa, a special thanks to you my angels for being my source of inspiration and always encouraging mommy to always do her best. My life is incomplete without you.

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"I Can Do All Things Through Christ Who Strengthens Me" (Philippians 4:13)

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ABSTRACT

Water is the source of life because all living organisms cannot survive without it and it is the most important liquid in the ecosystem hence protecting water resources and ensuring water quality should always be an issue of the highest priority at the top of all environmental issues. Currently, both developing and developed countries are experiencing numerous water quality challenges. Among the challenges include lack of adequate water due to pollution as well as the management and disposal of oily wastewater effluents in water resources. Regarding the issue of pollution due to oily wastewater, the current trend shows that, with the increase in industrialization, the amount of oil used is also increasing, thus causing more stress in terms of management and treatment of wastewater. Oily wastewater pollution has mainly been reported to cause hazardous effects to both organisms and the environment by causing the deterioration of aquatic resources. This in-turn affect the quality of ground water, surface water, endanger human health, cause of atmospheric pollution, destroy/degrade natural landscape, and even cause safety issues due to the use of coalescence of the oil burner that arise. Due to this phenomena, various regulatory bodies have established some guidelines to regulate the disposal of oily wastewater that is discharged to the environment. Therefore, oily wastewater needs to be treated prior to being discharged into the environment to comply with state and local disposal regulations. Industries and companies that deal with activities that lead to the discharge of oily wastewater need to comply to the enforced regulations to ensure that the characteristic of their effluents meet the stipulated disposal criteria. The effluent quality requirements for discharge of oily wastewater to the municipal streams are determined by local and municipal authorities and, they may vary from place to place. This dissertation focused on the development of a model that can be used to indicate the quality of oily wastewater known as oil -produced water (OPW) which is normally discharged by petroleum industries to into receiving water bodies. The model development was accomplished by using a measure of evaporation patterns in relation to certain environmental and climatic variables. This is possible because certain physico-chemical parameters that normally characterize OPW are known to have a direct relationship with the rate and pattern of OPW evaporation. However, due to the complexity of the relationship between the parameters being measured, it was imperative to employ dimensional analysis approach that is based on Buckingham pi (π) theorem for the estimation of oil produced water evaporation

(OPWE) as a function of clear water evaporation (CWE) and influencing parameters. The parameters that were investigated in this project includes climatic and environmental parameters. The climatic parameters included wind speed (W), solar radiation (R) and air temperature (Ta). The environmental parameters were: oil produced temperature (Topw), electric conductivity (EC), total dissolved solids (TDS), biochemical oxygen demand (BOD), total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total petroleum hydrocarbons (TPH) and total organic carbon (TOC). The results have indicated that, the physico-chemical analysis for the samples from the oil depot (petroleum industry) were found to be within acceptable threshold limits except for COD, TPH and EC that slightly surpassed. These findings and observations from this work suggests that, wastewater from this oil depot that was studied should not be directly discharged into municipal channels, rivers, and streams unless it undergoes secondary and tertiary treatment processes. Alternatively, the wastewater may arrange for an agreement with the municipals to allow for their effluents to be channelled to local municipality streams where they will undergo further treatment since most depot do not have appropriate facilities for post-treatment process. This is because, the chemical effluent must also adhere to the guidelines and regulations of the municipal where the wastewater will be channelled into. Since most depots are not equipped with appropriate facilities to check for compliance prior to the discharge of the effluents, this work has developed a multiplicative model for such purposes. Nonetheless, modelling the OPWE for compliance purposes has received little attention thus far. Driven by this knowledge gap, this project focused on the development of a model to predict the compliance of OPW effluents for both checking of quality and attaining the regulatory compliance. The modeling approach was based on experimental data collected on the oil depot, South Africa for a period of six months. As a result of this analysis, a multiplicative model to formulate OPWE as a function of influencing parameters indicated a reasonably well accuracy (RMSE = 0.49) for the OPWE estimation. The evaporation and correlation study supported the hypothesis. As shown by the evaporation patterns that most of the time the effluent was compliant to the guidelines mostly during winter time than summer time, and this observation was explained by the evaporation patterns that in summer when there is more solar radiation, the wastewater absorbed more heat and enhanced the evaporation rates which is directly related to both environmental and climatic parameters. Furthermore, the model developed by this work, can be used for fingerprinting since OPWE from different processes

may have similar chemical composition but in different levels and ratios. This can be exploited to differentiate them using the same developed model as the coefficients pattern tend to be characteristic to a certain OPWE and the model can then be used to fingerprint and identify culprits in case of discrepancies.

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LIST OF ABBREVIATIONS

ANFIS	Adaptive neuro fuzzy inference system
ANN	Artificial neural network
BOD	Biochemical oxygen demand
BTEX	Benzene, toluene, ethylbenzene and xylene
COD	Chemical oxygen demand
CWE	Clear wastewater evaporation
DO	Dissolved oxygen
DWAF	Department of Water Affairs and Forestry
EC	Electrical conductivity
EPA	Environmental Protection Agency
Epan	Evaporation from the pan
GC	Gas chromatography
GC/FID	Gas chromatography with flame ionization detection
GC/MSD	Gas chromatography with mass spectrometric detection
GC-MS	Gas chromatography mass spectroscopy
GC-TOF-MS	Gas chromatography coupled to time of flight mass spectroscopy
GEP	Gene expression programming
HCl	Hydrochloric acid
HSE	Health, Safety, and Environment
LRB	Laboratory reagent blank
LOD	Limit of detection

LOQ	Limit of quantification
LCMS	Liquid chromatography-mass spectrometry
MAE	Mean absolute error
NaOH	Sodium chloride
O&G	Oil and grease
OPW	Oil-produced water
OPWE	Oil-produced waste evaporation
PAHs	Polycyclic aromatic hydrocarbons
R	Solar radiation
RMSE	Root mean absolute error
RSD	Relative standard deviation
SD	Standard deviation
S/N	Signal to ratio
T_a	Air temperature
TDS	Total dissolved solids
TOC	Total organic carbon
Topw	Oil-produced temperature
TPH	Total petroleum hydrocarbons
TSS	Total suspended solids
UNICEF	United Nations International Children's Emergency Fund
USEPA	United States Environmental Protection Agency
W	Wind speed
WHO	World health organization

WWE	Wastewater evaporation
WWTW	Wastewater treatment works

CHAPTER 1 : INTRODUCTION

1.1 **Background**

Water is an indiscipensable renewable natural resource that is essential to all living organism as it sustains life. However, due to the ever increasing population, industrialization, urbanization, and the technological advancement trend in general, this precious resource is continuously becoming under severe stress. A report by Charting Our Water Future suggested that by 2030, the water demand will exceed supply by 50% in some developing regions of the world, including South Africa, which is one of the water-scarce countries (Charting Our Water Future, 2009). Furthermore, according to the previous reports, by 2030 certain parts of Africa will significantly be affected to the extent that millions of its inhabitants expected to be living in areas of high water stress (Kusi *et al*., 2015).

In general, there are numerous factors, that contribute to water scarcity, and they include pollution, climate change and population explosion (MacDonald, 2010) and all these add strain the high demand of better water quality. In addition, there is an issue of the management of water quality which, if not addressed, could result in water becoming unavailable for many users. In recent years, the sources of fresh water in South Africa has been declining in quality because of an increase in pollution and the destruction of river catchment caused by deforestation, urbanisation, damming of rivers, destruction of wetlands, mining, industry, agriculture, energy use and accidental water pollution (Gambhir *et al.*, 2012).

Water pollution is any change in physical, chemical and biological properties that has repercurssions on life form (WHO,1997). A more serious aspect of water-pollution is that which is caused by human activity, including the impacts of industrialization and technological advancements that is one the increase in all sectors (Gambhir *et al.*, 2012).

Since water is essential for the sustainance of the planet earth and for the organisms to grow and prosper, it is imperative that appropriate measures are put in place to safeguard the sources of water and ensure that pollution is kept to the very minimum, if not completely eradicated.

However, there is a tendency to disregard this idea and in many occassions there has been delibarate tendencies of polluting sources of waters including rivers, oceans, and lakes. This will cause tremendous harm to both the environment globally as well as to the living organisms that will become negatively affected and at an alarming rate (Nkwonta and Ochieng, 2009). Due to the problems of water pollution, the entire ecosystem gets negatively affected.

The domestic wastes are normally among the major sources of water pollution. they include those that are produced by households in the kitchens, laundry washings, as well as those that come from sewage or septic tank leakage and which end up contaminating natural waters. The domestic wastes also include those that oigininate from the use of fertilizers that are used extensively in household lawns and gardens.

Agricultural waste is another source of water pollution; because this activity involves the application of commercial agrochemicals and fertlizers during the cultivation of crops and/or they are used in animal husbandry. Worldwide, agriculture is among the leading sources of soils and sediment pollution because it involves ploughing and other activities that remove plant cover and disturb the soil (Busari et al., 2015). Agriculture is also a major contributor of pollution due to residues of organic chemicals, especially pesticides (Gambhir *et al.*, 2012). In most countries throughout the world, commercial persticides are still used extensively in morden agriculture in a wide range of environment. .However, environmental monitoring schemes has increasingly indicated that trace amounts of pesticides are still being detected in surface and underground water bodies, even far from the sites of pesticide application (Voltz, Louchart and Andrieux, 2003).

Industrial waste is another huge source of pollution problems in the environment. It refers to the waste that is produced during industrial processes and activities and may include any material rendered useless during or after the manufacturing processes (Voltz, Louchart and Andrieux, 2003). And the issue of concern is that, amongst the major sources of environmental pollution is industrial effluents that contaminate the water bodies (Kaur *et al.*, 2010). Balasubramani and Sivarajasekar, (2018) reported that, petroleum industry is one of the major sources of industrial effluents affecting the environment. Due to this, there is a need to investigate the quality of

wastewater discharged from petroleum industries and if they comply to the stipulated regulatory guideline standards. Wastewater emanating from petroleum processes and produced water tends to contain chemical ingredients that are persistent in the environment and this happen to be a challenge for the industry as they seek to minimize their impact on the environment. Since oily wastewater known as produced water is the largest waste stream from oil fields, it is imperative to monitor and check its compliance in terms of the chemical composition of the effluent prior to it being discharged to the receiving bodies. This is important because the entrance of the untreated produced water to the receiving streams tends to cause water pollution. The sources of the pollution due to produced water include runoffs, marine vessels, accidental spills and operational discharges from offshore oil and gas activities (Fraser, Russell and Zharen, 2006; Carpenter, 2019).

South Africa is one of the water scarce countries and water pollution plays a significant role in reducing the number of freshwater resources available to humans (Muller *et al.*, 2009). Industrial wastewater released into water bodies contribute to the water scarcity experienced by the country since it introduces chemical species that deteriorate the quality of water rendering it unfit for human consumption (Kaur *et al.*, 2010). The discharge of untreated or partially treated produced water from oil and gas industries into receiving water bodies has caused the alteration and quality degradation of the environmental water making it not suitable for any human use (Ganoulis, 2009). As previously defined, the oily wastewater generated from oil and gas exploration activities is termed as oil- produced water (OPW) implying that the oil is produced along with water. Hence, the chemical composition of the OPW to be discharged into the receiving body need to ensure that it meets the stipulated criteria enforced by regulatory agencies. To ensure compliance, the industrial effluents need to be analyzed frequently and this is laborious, uneconomical and may even lead to secondary pollution due to the hazardous chemicals and materials depending on the method used during the physico-chemical analysis of the effluent. Therefore, the main aim for this project was to investigate the possibility of using the evaporation patterns of OPW to develop a reliable and predictive model that can be used to indicate cases of non-compliance for the effluents discharged from industries that deal with petrol and petroleum products specifically. This is possible because the magnitude of certain parameters normally present in oily wastewater has a direct mathematical relationship with the

rate and patterns of evaporation. Since the study of evaporation has been reported by various researchers and has been applied to solve different issues related to the water crisis (Coleman, 2000; Chakraborty, Hiremath and Sharma, 2017) , it seemed plausible to use a similar approach to achieve the aim of this study. Furthermore, Robinson, (1973), Davis *et al*, (1973), Parker *et.al*, (1999) all attempted to apply the concept of the percentage of clear water evaporation (CWE) to wastewater evaporation (WWE) in order to estimate wastewater evaporation rates however this study yielded varying results.

The development of mathematical relationships for variables that control the rate and patterns of oil-produced water evaporation (OPWE) against the evaporation of clear water (CWE) will be used to deduce a predictive tool that will indicate whether or not there is compliance of the OPW to the stipulated guidelines. There are many ways of developing such kind of mathematical relationships and one such approach that will be employed in this work does utilize the principles of dimensional analysis. This approach is very attractive as it makes use of parametric units to generate a model for the parameters being investigated. Once the model is generated, it will be suitable and appropriate for that particular environment.

1.2 **Problem Statement**

The physical and chemical properties of OPW vary significantly depending on the geologic formation of the underlying rocks, geographic location of the field, and the type of hydrocarbon product being produced (Clark and Veil, 2009). There are various approaches to manage OPW and these include, reuse of the water if certain water quality conditions are met, however, OPW generated is normally discharged to the receiving bodies and are subject to applicable regulatory requirements. Another approach of managing produced water involves underground injection of OPW for disposal through injection wells thus increasing oil recovery, evaporation of water from the surface and enabling beneficial reuse, such as for livestock watering, crop irrigation, wildlife, aquaculture, watering and habitat, and hydroponic vegetable cultivation (Clark and Veil, 2009). However, the salinity of the OPW imposes a significant challenge for agricultural purposes because crops vary in their susceptibility to salinity, and when salinity rises above a threshold for a species, the crop yield will decrease. Not only the quantity but also the quality of the OPW has

important implications for the management of agricultural activities as well as influencing the total dissolved solids (TDS) which is one of the important quality parameters to be considered. Due to the limitations of the approaches for the management of OPW there is a need to come up with a more sound approach to address the issue of the compliance to the discharges emanating from OPW industries. The use of dimensional analysis to develop mathematical models that will predict the level of compliance of OPW discharges to the receiving bodies using both physico-chemical and environmental variables may prove to be very relevant and sustainable.

1.3 **Justification**

Water is an essential component of life and it gets degraded in quality when it contains an excess of unwanted chemicals and harmful pathogenic microorganisms. Currently, due to the exponential economic development, and industrial growth, there is an increasing demand for oil worldwide. This high demands for oil come with challenges related to the treatment and disposal of the generated oily wastewater. Contamination of oily wastewater is responsible for serious environmental degradation and pollution as the oily wastewater enter municipal streams and eventually get into the municipal wastewater treatment plants. The municipal wastewater treatment plants then become overburdened as most of them were designed to treat nutrients and other organic pollutants of domestic origin, but they were not designed to treat oil produced wastes which are highly toxic. Due to the negative consequences of the chemical components present in oily wastes to the ecosystem, aquatic organisms and the environment, the discharge of OPW is regulated. Therefore, industries and companies that deal with activities that lead to the discharge of oily wastes need to comply with the regulations which are enforced to them by authorities in order to ensure that the characteristic of their effluents meets the stipulated criteria. Compliance needs to be addressed by putting in place concrete and sustainable strategies for the monitoring of the characteristics of the oily wastewater effluents. To check compliance, the wastewater needs to be verified in accordance to the standard analytical procedures, however, among the drawbacks associated with this consideration is that some of the industries do not have special equipment to check and verify the compliance.

Therefore, this dissertation aimed at developing a mathematical model that can be used to indicate cases of non- compliance by using evaporation patterns of OPW. However, due to the

complexity of the relationships between the variables that were collected, the model was derived using dimensional analysis based on Buckingham π theorem (Buckingham, 1914) for estimating oil-produced evaporation (OPWE) as a function of clear water evaporation (CWE) and climatic parameters. The choice of dimensional analysis based on Buckingham π theorem is supported by the fact that it has the ability to reduce complex physical problems in a simple form before obtaining a quantitative answer and the method is of great generality and mathematical simplicity. It is the concept of similarity which refers to some equivalence between two things, processes or phenomena that are different with respect to nature or scale, processes or phenomena (Flaga, 2015). Therefore, it is imperative to use this tool to find the relationship between the dependent parameter (OPWE) and independent parameters (environmental and climatic). The parameters that were investigated in this project included climatic parameters: wind speed (W), solar radiation (R), air temperature (Ta) and environmental parameters: OPWE, CWE, oil-produced temperature (Topw), electric conductivity (EC), biochemical oxygen demand (BOD), total dissolved solids (TDS), total suspended solids (TSS), chemical oxygen demand (COD), total petroleum hydrocarbons (TPH) and total organic carbon (TOC). The comparison of a mathematical model with experimental data served as a means of validation of this study.

1.4 **Aims and Objectives**

1.4.1 **Aims**

The main aim of this study was to use dimensional analysis to develop a model that can be used as an indicator of oily wastewater pollution, fingerprinting, and compliance.

1.4.2 **Objectives**

The objectives of this study were:

- To investigate the influence of oily wastewater parameters (TSS, COD, BOD, TPH, EC, Topw and TOC) on evaporation of wastewater by using Class A pans.
- To investigate the influence of climatic parameters (Ta, W, and R) on OPWE.
- To develop a model that can be used as an indicator of oil produced water pollution and compliance of its discharge.
- To use the developed model to fingerprint and identify culprits in case of discrepancies.

1.5 **Dissertation outline**

This chapter (**Chapter 1**) provided the background of the identified research problem and also defined the objectives of the study.

Chapter 2 reviewed the available literature on effluent quality requirements for the discharge of produced water receiving bodies. This chapter also studies in detail certain parameters investigated in this project and their maximum permissible amounts according to regional and local authorities. Methods for estimating open water evaporation, meteorological factors affecting evaporation and properties of the water body affecting evaporation was also be reviewed in this chapter.

Chapter 3 provided a detailed description of the methodology and procedures to achieve the research objectives of this project. All the experimental and analytical procedures carried out, features of the list of material used and the analytical technique used.

Chapter 4 dealt with the identification of total petroleum hydrocarbons (TPH) in oil produced water (OPW) samples. Different types of TPH identified using the NIST database as well as the fragmentation pattern of the GC-TOF-MS are presented and discussed.

Chapter 5 discussed the influence of environmental and climatic factors on the evaporation rate of wastewater. The interdependence between these parameters and how the influence the rate of evaporation of the OPW with respect to the clear water is presented.

Chapter 6 dealt with the use of dimensional analysis to develop a model to predict quality and compliance of oily wastewater discharged onto municipal channels

Chapter 7 is about conclusion and recommendations that may be relevant in the future for the continuation of the work that may result into the models that will be applicable to other types of OPW.

1.6 **References**

Arthur, J. D., Langhus, B. G. and Patel, C. (2005) *Technical summary of oil & gas produced water treatment technologies*.

Balasubramani, K. and Sivarajasekar, N. (2018) 'A short account on petrochemical industry effluent treatment', *International Journal of Petrochemical Science & Engineering*, 3(1), pp. 10–12. doi: 10.15406/ipcse.2018.03.00070.

Buckingham, E. (1914) 'On physically similar systems; Illustrations of the use of dimensional equations', *Physical Review*, 4(4), pp. 345–376. doi: 10.1103/PhysRev.4.345.

Busari, M.A., kulal, S.S. Kuar, A. Bhatt, R. and Dulazi, A.A. (2015) ' Conversation tiallage impacts on soil , crop and the environment', *International Soil and Water Conversation Research*, 3, pp. 119-129.

Carpenter, A. (2019) 'Oil pollution in the North Sea : the impact of governance measures on oil pollution over several decades', *Hydrobiologia*. Springer International Publishing, 845(1), pp. 109–127. doi: 10.1007/s10750-018-3559-2.

Chakraborty, P. R., Hiremath, K. R. and Sharma, M. (2017) 'Evaluation of evaporation coefficient for micro-droplets exposed to low pressure : A semi-analytical approach', *Physics Letters A*. Elsevier B.V., 381(5), pp. 413–416. doi: 10.1016/j.physleta.2016.11.036.

Charting Our Water Future (2009) *Charting Our Water Future Economic frameworks to inform decision-making*, *Water*.

Clark, C. and Veil, J. (2009) *Produced Water Volumes and Management Practices in the United States*, pp. 1-64.

Coleman, M. (2000) *Review and Discussion on the Evaporation Rate of Brines*, *Members.Iinet.Net.Au*. Available at: http://members.iinet.net.au/~actis/evaporation_rate_of_brines.pdf.

Flaga, A. (2015) 'Basic principles and theorems of dimensional analysis and the theory of model similarity of physical phenomena', in *Technical Transactions Civil Engineering*, pp. 241–272. doi: 10.4467/2353737XCT.15.135.4172.

Fraser, G. S., Russell, J. and Zharen, V. (2006) 'Produced water from offshore oil and gas installations on the grand banks , new found land and labrador : are the potential effects to seabirds sufficiently known ?', *Marine Ornithology*, 34, pp. 147–156.

Gambhir, R. S., Kapoor, V. Nirola, A. Sohi, R. and Bansal, V. (2012) 'Water Pollution: Impact of Pollutants and New Promising Techniques in Purification Process', *Journal of Human Ecology*, 37(2), pp. 103–109. doi: 10.1080/09709274.2012.11906453.

Ganoulis, J. (2009) *Risk Analysis of Water Pollution. 2nd ed.; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany*.

Kaur, A., Vats,S. Rekhi, S. Bhadwaj, A. Goel, J. Tanwar, R.S. Gaur, K.K. (2010) 'Physico-chemical analysis of the industrial effluents and their impact on the soil microflora', in *Procedia Environmental Sciences*, 2, pp. 595–599. doi: 10.1016/j.proenv.2010.10.065.

Khatib, Z., and Verbeek, P. (2003) 'Water to Value — Produced Water Management for Sustainable Field Development of Mature and Green Fields' J*ournal of Petroleum Technology*, pp. 26–28.

Kusi, L. Y., Agbeblewu, S. and Nyarku, K. M. (2015) 'Challenges and Prospects Confronting Commercial Water Production and Distribution Industry : A Case Study of the Cape Coast Metropolis', 5, pp. 544–555.

MacDonald, G. M. (2010) 'Water, climate change, and sustainability in the southwest', *Proceedings of the National Academy of Sciences*, 107, pp. 21256–21262. doi: 10.1073/pnas.0909651107.

Muller, M., Schreiner, B. Smith, L. Koppen, B. Sally Sally, M. Cousins, B. Tapela, B. van der Merwe-Botha, M. Kara, E. and Pietersen, K. (2009) *Water security in South Africa. Development Planning Division.*

Nkwonta, O. I. and Ochieng, G. M. (2009) 'Water Pollution in Soshanguve Environs of South Africa', *World Academy of Science, Engineering and Technology*, 56, pp. 499–503.

Robinson, D. (1973) ‘Differentials and incomes policy ‘’, *Economics and Statistics*, 4, pp. 4–20.

Shaffer, D. L., Chavez, L.H.A. Ben-Sasson , M. Castrillón, S.R. Yip, N.G. and Elimelech, M. (2013) ‘Desalination and Reuse of High-Salinity Shale Gas Produced Water: Drivers, Technologies, and Future Directions’, *Environmental Science and Technology*, 47, pp. 9569–9583.

Voltz, M., Louchart, X. and Andrieux, P. (2003) ‘Processes of pesticide dissipation and water transport in a Mediterranean farmed catchment’, *IAHS-AISH Publication*, (278), pp. 422–428

WHO (1997). Water Pollution Control - ‘A Guide to the Use of Water Quality Management Principles’. Great Britain: WHO/UNEP.

CHAPTER 2 : LITERATURE REVIEW

This chapter focuses on the survey of the literature related to the effluent quality requirements for discharge of OPW to the municipal sewerage systems and the compliance to the stipulated guidelines, regulations and laws enforced to companies and other entities that deal with oil produced water directly. This chapter also surveys in detail the development of various models that have been reported for wastewaters, their derivation, usefulness, and performance. Moreover, the chapter points out the gaps that exist to-date and of which; this project has invested efforts to address.

2.1 **Environmental concerns of discharge of oily wastewater**

The discharge of oily wastewater is currently a serious challenge to the petroleum industries (Jamaly, Giwa and Hasan, 2015; Varjani *et al.*, 2019). Normally, the chemical composition of the wastewater to be discharged into the receiving bodies need to ensure that it meets the stipulated criteria enforced by the regulatory agencies. Oily wastewater refers to wastewater mixed with oil under a wide range of concentrations and its composition includes a heterogeneous mixture containing several components such as different types of oils, light hydrocarbons, heavy hydrocarbons, surfactants from detergents, metals etc. (Yu, Han and He, 2017). Oily wastewaters are generated from a variety of industries such as petrochemical industries, oil refinery, oil transportation as well as oil exploration (e.g., fracking) and is usually produced as undesirable by-products which in industries are known as “produced water” (Igunnu and Chen, 2014). The types and concentrations of contaminants that characterize produced water originating from different sources tend to differ greatly and the contamination of water sources by oily materials is a huge global challenge.

Even though oil and water do not mix, they can, however, co-exist in a form known as an “emulsion” (a mixture of two or more liquids that are normally immiscible). If the emulsion is left to settle, the two components will tend to separate because of the differences in density. With the increase in industrial processes and other economic activities, the demand for oil has as well been on the increasing proportionally, thus an increase in the oily wastewaters which in turn

cause stress in terms of various technical and management developments leading to oily wastewater pollution (Yu, Han and He, 2017).

2.2 **The impact of pollution from the oil depot**

The oily wastewater covers a broad range of organic toxic wastes which are mainly produced in oil refinery, oil processing, transportation, and petrochemical industry and also oil depot as a result of oil spill (Ahmed, El-Sayed and El-Saka, 2007; Machín-Ramírez *et al.*, 2008; Alzahrani and Mohammad, 2014; Silva *et al.*, 2014; Yu, Han and He, 2017; Munirasu, Haija and Banat, 2016). With the global population increasing, there is an increase in industrial activities that lead to an increase in the amount of oil used which may result in a larger-scale of environmental pollution by oil spills involving, leakages from tanks, blowouts, and dumping of petroleum products waste into the environment. The after-effects of such activities have been widely reported (Adeniyi and Afolabi, 2002; Adeniyi, Yusuf and Okedeyi, 2008; Adewuyi and Olowu, 2012). In most oil depots there is no thorough processing or other meaningful transformation on site. Most of the time the product reaching the depot (from the refinery) is in the final form suitable for delivery to the end-users. The key factor is Health, Safety, and Environment (HSE) whereby the depot's operators see to it that products are safely stored and handled that is, there are no leakages from tanks or pipes which could lead to damage to the water table or soil. In case of spillage incident at the depot, there are various types of mechanical devices to collect, contain, recover oil from the water surface detected by the surveillance and normally, boom and skimmers are used. The recovered oil is stored temporarily in built in tanks, on deck storage containers. However, there are factors that may affect the effectiveness of the mechanically recovery which include, weather conditions, spreading and water state.

2.3 **Oil produced water from oil production**

As previously stated, oil produced water (OPW) is a term that is mostly used by industries that refers to the water containing oil as a by-product during oil and gas exploration. It is the largest waste stream emanating from petroleum production operations (Ahmadun, Pendashteh and Chuah, 2009; Isehunwa and Onovae, 2011; Al-Kaabi *et al.*, 2019). OPW is described as water trapped in underground formation that is brought into surface during oil and gas exploration and

production. Since the water has been in contact with the hydrocarbon bearing formation for centuries it, therefore, carries some of the chemical components associated with the formation of hydrocarbon. The term OPW may include water from the reservoir, water entrapped in the formation and chemicals added during the oil or gas production and treatment process. It is a complex mixture of organic acids, hydrocarbons, heavy metals, phenols, and oil production chemicals (dissolved and dispersed) (Røe Utvik, 1999; Thomas *et al.*, 2009). In other countries including the Gulf of Oman, the produced water is stored in treatment lagoons before discharging to the receiving bodies. However, before they discharge, the physico-chemical composition of the produced water effluent is recorded to satisfy the demand for compliance with the stipulated discharge guidelines and regulations. The effluent discharge guideline standards are the maximum allowable concentration limits of particular parameters in industrial wastewater that can be directly discharged into the receiving streams/bodies. These permissible concentration limits are meant to enforce the regulatory guidelines to the companies, entities and industries that deal with activities that has the potential to lead to the discharge of produced water to the environment and thus prevent any possible pollution.

2.4 **Regulations of the discharge of produced water.**

In terms of the regulatory framework, the chemical composition of the OPW to be discharged to the receiving bodies need to comply with the criteria set by the authorities or regulatory agencies such as Governments and International agencies. This criterion does set the maximum permissible limits and the permitted limits may vary from one country to another depending on various factors. In Indonesia for example, the effluent discharge limit for oil and gas (O&G) differ based on different types of oil industries whereby 30 mg/L of O&G is set as maximum limit for palm oil industries, 25 mg/L is stipulated for oil refining and urea fertilizer and 5.0 mg/L is set for leather tanning and textiles (Abdullah BT, 2016). For offshore in Australia, the permitted limits for O&G are 30 mg/L daily average and 50 mg/L instantaneous (Hedar & Budiyono, 2018). According to the United States Environmental Protection Agency (USEPA) regulations, the maximum permissible limit standards for O&G is set at 42 mg/L for daily allowable maximum concentration and the monthly average is set to be 29 mg/L (Ahmadun, Pendashteh and Chuah, 2009). The convention for the protection of the marine world of the North-East Atlantic has set the maximum limit standard of dispersed oil for produced water into

sea to be 40mg/L (Ahmadun, Pendashteh and Chuah, 2009). Due to environmental concerns, most countries have imposed uncompromising regulatory limits for the discharging of the produced water. Table 2.1 shows the limits of different countries including South Africa.

Table 2.1: Limit of oil and grease for different countries including South Africa.

Country/State	**O&G (mg/L)** **Daily**	**Monthly**	**Reference**
South Africa	-	2.5	(Government Gazette, 1984) (Department of Water Affairs., 2013)
United State of America (USA)	15	12	(Abass O *et al.*, 2011)
Nigeria	-	10	(Isehunwa and Onovae, 2011) (Nkwocha *et al.*, 2013)
New Jersey	15	10	(Alther, 2008)
Wyoming	-	10	(Alther, 2008)

2.5 **Environmental effect of petroleum pollution to the environment**

Generally, there is more in OPW in terms of their chemical composition than just oil and water. Isehunwa and Onovae (2011) reported that there is a presence of nickel, silver, zinc, iron, lead, and also small amounts of natural radioactive materials. Moreover, the composition of OPW

from different sources or industries does vary by a certain order of magnitude. Environmental concerns have driven the research into ensuring the quality of OPW effluent discharged into the environment meet the stipulated standards. This is because, it is not only affecting the surrounding location of the industry but also end up affecting the aquatic ecosystem located even far away from the industry due to water flow which can transport such contaminants from the original source. The main pollution challenge associated with the OPW is that it can lead to the formation of the oil layer on top of water surface, which leads to the reduction of the light penetration thus tempering with the process of photosynthesis which directly affect aquatic plant growth (Abdullah, 2016). It also affects the survival of the aquatic ecosystem by hindering the oxygen transfer by diffusion from the atmosphere to water which significantly reduce the amount of dissolved oxygen in water (Agrawal and Sahu, 2009). Regarding discharging into municipal wastewater treatment works (WWTW), the regulations enforce companies to pre-treat the effluent in their schemes before channeling these industrial OPW into municipal channels. This has been enforced in order to prevent damage to the WWTW infrastructure and any negative disadvantageous effects on the environment and ecosystem (National guideline_Land based influent_Discharge coastal, 2014). Therefore, it is imperative to analyze the OPW to ensure that no negative impacts that can affect aquatic species, ecosystem, or environment. The importance of measuring OPW is that the measurements can be used to optimize the treatment process and can also play a role in ensuring regulatory compliance. Other benefits will include the possibility of generation and collection of data that will allow regulators and the oil companies to establish better environmental practices and to know precisely how much the wastewater has been discharged and enabling the possibility to come up with the better treatment processes and disposal.

Proper management of OPW should start from accurate measurements and estimation of the actual volume produced. Large quantity of wastewater requires an appropriate treatment before being discharged into the environment. It must be treated prior to being discharged into receiving water bodies since such water usually contains dissolved and suspended matter that will temper with the quality of water. The characteristics of the effluent in question should be defined precisely and the quality should be examined before discharging into the aquatic environment or to be treated and reused. This is essential for setting baseline conditions and standards.

2.6 **Characteristics of oil Produced Water**

Quantitative assessments of the quality of the OPW are made by considering the following parameters:

2.6.1 **Water Temperature**

Temperature is a very important parameter because of its influence on the water chemistry. Normally, the rate of chemical and biological reactions increases with temperature. It is also important to aquatic life as many biological processes such as enzymatic processes are highly dependent on temperature which in turn affects biological activity. The temperature can be measured using a thermometer and is expressed in °C units. Water temperature is an important quality parameter to measure prior to the water being discharged into rivers and streams. This is because; the temperature of water has the direct effect on all the organisms that are in it. Each organism has its optimal temperature range to require for survival and thriving. For example, cold water species have physiological temperature optimums <20 °C, cool water species have physiological temperature optimums between 20 and 28 °C (Magnuson *et al.*, 1997; Rahel and Olden, 2008).

2.6.2 **Total suspended solids (TSS)**

The total suspended solids (TSS) refers to particles large enough to be retained in a filter device of pore size 2 μm or less. TSS is usually determined by the filtration process using a vacuum filtration unit with glass fiber filters. A high level of TSS may settle out onto a lake or stream-bed bottom and cover aquatic organisms' eggs, or macro-invertebrate larva (Whitman College, 2015). This coating can prevent the required oxygen transfer and result in the death of buried organisms. Its formation is dependent primarily on physical processes driven by hydrological factors. TSS also decreases the effectiveness of drinking water disinfection agents by allowing the microorganisms to "hide" from disinfectants within solid aggregates (Whitman College, 2015). Hence, the turbidity or TSS is removed in drinking water treatment facilities.

2.6.3 **Total dissolved solids (TDS)**

Total dissolved solid (TDS) refers to the total measurement for organic matter, inorganic salts as well as other dissolved materials present in water (Butler and Ford, 2019; Gupta, 2011). It is generally measured using gravimetric techniques by weighing the residue remaining following evaporation of a known volume of the filtered sample. For rapid test, it can be determined using the conductivity/TDS meters and is expressed as of mg/L. On the other hand, it can be obtained indirectly by summing up the measured concentrations of constituents in the filtrate. Alternatively, TDS can be estimated from conductivity (μS/cm) measurements by multiplying with an empirical determined conversion factor ranging from 05 to 0.9. The exact factor is determined through linear regression of repeated paired measurements of specific TDS and conductance and it depends on the solution's composition. Nonetheless, for most natural water systems, 0.67 is used often when the exact conversion factor is not known (Gupta, 2011 Weiner, 2013).

2.6.4 **Electrical conductivity (EC)**

Electrical conductivity (EC) is the measure of the ability of the solution to conduct electric current a property immensely dependent on the availability of ionic species (Trick, Smart and Reeder, 2008). EC is directly proportional to a TDS measure. Basically, high levels of EC in wastewater indicates high TDS concentration. This also implies that the concentration of ionic solutes dissolved in water is directly proportional to the ability of an ability of an electric current to pass through the wastewater (Atekwana *et al.*, 2004) and therefore EC helps to indicate the purity of water. The purer the water, the lower the EC this means that there are low levels of ions to conduct electricity.

2.6.5 **Biochemical oxygen demand (BOD)**

Compounds containing organic matter can be measured in simple parameters which are biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic matter (TOC) (Samudro and Mangkoedihardjo, 2014). BOD is an empirical test referring to the measurements of the amount of the oxygen that the bacteria will consume while decomposing biodegradable organic matter under aerobic conditions. It is an indirect measure of the level of organic contamination in water and is measured in mg/L. The BOD test does not oxidize all the organic matter present in the water but only the organic matter that are biochemically degradable

during a specified incubation period which is 5 days at 20°C. BOD is set to be an indicator of the quantum of pollution load. If the load of pollution is high therefore, there will be less DO in water that is, greater amount of DO shall be consumed. Low values of BOD indicates relatively pure water whereas high BOD results in harming the aquatic species (Naubi *et al.*, 2016) hence it is an important water quality parameter to measure.

2.6.6 **Chemical oxygen demand (COD)**

The chemical oxygen demand (COD) is a standard test for water which uses a strong chemical oxygen oxidizing agent (potassium dichromate) to chemically oxidize organic matter and inorganic chemicals in the sample of wastewater for a few hours, (normally 2 hours) under conditions of heat and strong acid . The potassium dichromate is not specific to oxygen-consuming chemicals either organic or inorganic and therefore, both chemicals are included in a COD measure. It is a laboratory assay that measures the amount of organic matter (biodegradable and non-biodegradable) in a sample and it is measured in mg/O_2 equivalent /L. The COD values of a water sample can be related to the BOD value in more or less constant value. Since the COD test can be performed rapidly, it has an advantage (digestion in two hours) in comparison to BOD_5 (needs a minimum of five days incubation). COD test can also measure some additional organic matter such as cellulose, which normally cannot be biologically oxidized; hence, COD value is usually greater than that of BOD because more organic compounds can be chemically oxidized than biologically oxidized. Therefore, it is important to keep the COD with water quality standards because high values of COD stresses aquatic organisms which can even lead to death (Naubi *et al.*, 2016)

2.6.7 **Total organic carbon (TOC)**

TOC refers to the total content of organically bound carbon in dissolved and undissolved compounds and it is expressed in mg/L. Organic matter present in water can be measured by use of TOC test , which is especially applicable to small concentrations of organic matter. Organic carbon comprises nearly all carbon compounds except those carbon species which are viewed as inorganic (carbon dioxide, hydrogen carbonate, carbonate, cyanide, and some further examples which are not commonly found in wastewaters). The whole sample is normally subdued to oxidation (commonly by incineration of a known volume of the wastewater sample in the presence of a catalyst at 900°C using CO_2-free air) for detection of organic carbon in aqueous

samples. It is important to check compliance of TOC because in drinking water, the organic matter reacts with chemicals used for disinfection such as chlorine which can form disinfection by-product which can be carcinogenic.

2.6.8 **Quantification methods for organic matters**

Spectrophotometry is one of the methods used for quantitative analysis in different fields physics, chemistry, biochemistry, chemical engineering, material, and clinical applications. It measures the amount a chemical substance absorbs light as a beam of light passes through the sample solution. The spectroquant spectrometer has been used by many researchers for quantitative analysis (Yang *et al.*, 2007; Ignacio, Gernjak and Oller, 2008; Coban *et al.*, 2015). This is a colometric method which converts the component of a sample to be analyzed into a coloured compound in a specific reaction by means of reagents included in the self-test kits. This colour reaction method is an optimized approach based on standardized analytical methods. It is optimized in terms of low working effort, easiness of use and shorter reaction times. With spectroquant spectrophotometer method, the absorbance (which is measured by the intensity of the color of a solution) is directly proportional to the concentration of the respective analyte.

2.6.9 **Total petroleum hydrocarbons (TPH)**

OPW being a complex mixture of organic and inorganic compounds has total petroleum hydrocarbons (TPH) as one of the components and this parameter is usually important to be analyzed including its characteristics for produced water. The effluent from refineries and petroleum industries mainly contains oil, organic matter and other compounds (Kanu and Achi, 2011; Kulkarni and Goswami, 2015). A large family of compounds that originally come from crude oil are known TPH. It is useful to measure the total amount of TPH at the site since it is not practical to measure each one separately because there are many different chemicals that are present in crude oil. The amount of TPH found in a sample is useful as a general indicator of petroleum contamination at the site. Crude oil is used to make petroleum products and is known to contaminate the environment (ToxFAQs, 1999; Aljuboury *et al.*, 2017).TPH is a mixture of chemicals and all of them contain mainly hydrogen and carbon, and such compounds are termed as hydrocarbons. Among chemicals found in TPH are benzene, hexane, jet fuels, toluene, naphthalene, xylems, fluorine, as well as other petroleum products and gasoline components. However, not all of these occur in any one sample, but an individual sample will contain some or

as a mixture of some of these chemicals. To prevent water pollution, it is important to monitor all these parameters including TPH.

Sources of TPHs are many and broad; with some having their sources from the marine environment, some from anthropogenic (pyrogenic or petrogenic) sources and some having their origin from natural (diagenetic or biogenic) sources. Hydrocarbons which are produced by living organisms or through biological processes for example; processes mediated by algae, planktons, and bacteria or those involving terrestrial plants are known as biogenic sources (Tran, Yu and Zeng, 1997; Commendatore, Esteves and Colombo, 2000). Of the hydrocarbons, aliphatic hydrocarbons (C23-C33) are largely produced by the terrestrial plants (Kettler and Papastavros, 2000) whereas C15, C17, and C19 (odd number) n-alkanes are produced by biogenic marine input and mostly in low quantities (Iwegbue *et al.*, 2016). Diagenetic sources are those hydrocarbons which are produced as a result of a geochemical and physical changes gone through by sediment after its initial deposition as it changes into rock and enters the marine water usually by natural seepage (Commendatore, Esteves and Colombo, 2000). Hydrocarbons from anthropogenic sources are mostly generated from several human activities such as transportation, urbanization, industrialization, operations and storage, oil utilization, fishing and shipping. Kvenvolden and Copper (2003) and Sakari *et al.*, (2014) reported that abundance of C16, C18, and C20 mostly suggests oil spillage from oil pipe lines and tanks used for transferring oil from one place to another. It has been reported in literature that TPH concentrations are extremely high in industrialized areas and spillage sites (Adeniji, Okoh and Okoh, 2017) and amongst other factors contributing to the presence of crude oil in the marine environment about 63% arise from atmospheric emission, urban and river runoffs, as well as municipal and industrial discharges. Due to this, there is a need for ensuring compliance with the environmental laws related to transportation, oil exploration and discharge into marine environment for aquatic and human safety.

2.7 **Analytical methods for the determination of TPH in water**

The analytical methods for TPH involve several steps mainly sample preparation, separation, and detection.

2.7.1 **Sample pre-treatment methods for TPH**

Sample preparation generally refers to how a sample is treated prior to its analyses to exclude interfering species from the sample matrix and also set free the target analytes before their introduction to the analytical detection system. It is crucial and most important step in most analytical procedures because otherwise the signal of the target analytes will become masked by interfering species. Sample preparation may include sub sampling, chemical reaction with some species, dissolution, filtration, extraction or enrichment and pre-concentration procedures. Appropriate sampling procedure is very crucial to obtaining the correct analytical results where the aim is to get wholly representative sample from the environmental medium where it was collected (Weisman, 1998; ATSDR, 1999) because the aqueous sample to be analyzed can display varying concentrations in different places at different times. For this reason, OPW being a complex matrix it thus necessitates that a cleanup and/or enrichment of analyses be performed. Several clean-up protocols have been reported for OPW and they include solid phase extraction (SPE) (Yang *et al.*, 2011; Morris, Sellaro and Sarver, 2015), solid phase micro extraction (SPME) (Ilavsk and Hriv, 2004), vortex extraction (Suratman, 2013) and continuous liquid-liquid extraction (LLE) (Weisman, 1998; LLE EPA 3510) .

Each of these methods has its own advantages and disadvantages. For example, SPE uses the cartridge which contain an adsorbent such as alumina or silica in which the analytes are retained during the SPE percolated and the analytes are then eluted with the small volume of an appropriated organic solvents. The advantage of this method is that it uses the small volumes of solvents and less glassware and has great efficiencies. However, with SPE the sorption process of analytes fiber tends to compete with analytes sorption on suspended matter surface.

LLE which is a traditional solvent extraction method uses large volumes of organic solvents thus making it uneconomical and compromises with environmentally friendly techniques as large volumes of organic solvents will end up being disposed to the environment. Moreover, it is labor intensive and laborious. After the LLE extraction procedure, the organic phase is collected and concentrated prior to the instrumental analysis. In addition to the consumption of large volumes of solvents, solvent extraction requires a lot of glassware's (Huddleston *et al.*, 1998; Suratman, 2013 Ahmed, Mahmoud and Mousa, 2015; Morris, Sellaro and Sarver, 2015; Adeniji, Okoh and Okoh, 2017)

2.7.2 **Separation and detection methods for TPH**

After the clean-up step, a mixture of analyte in the extract must be separated before their introduction to the detection system because; when the analytes are introduced to the detector simultaneously, they may cause interference or musk one another. Among analytical methods used for TPH, the most commonly used include Raman spectroscopy, infrared (IR) spectroscopy, fluorescence spectroscopy (Muthukumar *et al.*, 2013; Okparanma and Mouazen, 2013) gravimetry, gas chromatography with mass spectrometric detection (GC/MSD) (Reddy and Quinn, 1999) , gas chromatography with flame ionization detection (GC/FID) (Suspes *et al.*, 2012), ultraviolet spectrophotometry, and immunoassay (IMA) (Okparanma and Mouazen, 2013). In addition, Reddy and Quinn, (1999) developed a Gas Chromatography-Mass Spectrometry (GC-MS) method for measuring both the polycyclic aromatic hydrocarbons (PAHs) and TPHs for seawater samples that were collected after the North Cape oil spill. LLE method was employed using methyl chloride as a solvent extraction. The signal from the ion m/z 57 ($C_9H_4^+$) which was a major ion in aliphatic compounds was integrated throughout the chromatogram and used to calculate the amount of TPHs. In another study, quantification of TPH using 5-α-androstane internal standard with a GC-MS analysis using a selected ion monitoring (SIM) mode to improve the detection limits (Yang *et al.*, 2011).

2.8 **Gas Chromatography-Mass Spectrometry**

Gas Chromatography-Mass Spectrometry (GC-MS) is a fundamental and complimentary part of many field studies involving organic compound detection and determination. GC and MS are two different techniques but are successfully coupled together to form GC-MS, simply because GC can separate many volatile and semi-volatile compounds but cannot selectively detect them whereas MS can selectively detect many compounds but not always separate them (Hussain and Maqbool, 2014).

2.9 **Evaporation principles**

Evaporation is a major component and it is one aspect that is less explained of hydrological cycle (Sudheer *et al.*, 2002; Salarpour *et al.*, 2014; Duffy, 2017) because it is not a simple phenomenon to explain as it requires numerous physical, chemical and meteorological variables to be explained. It is known as a physical process whereby a spontaneous escape of high energy

molecules from liquid surface into vapor state takes place and it occurs when a liquid is not in equilibrium with its vapor phase (Finch and Hall, 2001; Coleman, 2000) . The reverse process to evaporation for the liquid state is known as condensation. Evaporation from a water surface has been investigated by scientists since ancient times because it is an important process in the hydrological cycle (Pimentel *et al.*, 1997; Coleman, 2000; Roderick and Farquhar, 2002; Jensen, 2014). Estimates of evaporation from open water are used mainly for water balance studies to support appraisals of applications for abstraction licenses, in wetlands and still waters management, and has the potential to be used in modelling work in future (Finch and Hall, 2001). These estimates are increasingly required for several Environment Agency functions, particularly Water Resources and Ecology (Kusangaya *et al*., 2014; Bent, 2017). It is projected that the increase of approximately 40% in evaporation due to climate change is enough to influence the outflow of reservoirs significantly, due to the increase in temperature (Kusangaya *et al*., 2014; Bent, 2017).

Evaporation occurs at any temperature for different types of liquids and at different rates (Vuglinsky, 2009). The rate is controlled by the energy available at the water surface and the simplicity of the water vapor to mix in the atmosphere (Vuglinsky, 2009). Boiling differs from evaporation; in the sense that during boiling, vapor is formed not only on the surface but also inside the liquid and vapor bubbles go upward. Moreover, boiling occurs only at the temperature at which the pressure of the saturated vapor in the liquid attains the value of the atmospheric pressure. When the molecules of the liquid collide, they transfer energy to each other depending on how they collide (Vuglinsky, 2009). When a water molecule near the water surface absorbs enough energy to overcome the vapor pressure, it will escape in a gaseous form and enter the surrounding air above the water. As stated by the molecular-kinetic theory, evaporation is characterized by three phases that are interrelated and these are (i) evaporation of molecules from the evaporating surface; (ii) the absorption of some molecules by the evaporating surface and (iii) the diffusion of the remaining molecules into the surrounding space. Molecules in the inner water layers are affected by the attraction of the surrounding molecules, which is similar on average then move in any direction and at irregular intervals. Molecules at the surface water layer are affected by less attraction of the air molecules than the molecular attraction in the inner water layers due to the lower concentration of the air molecules. The ambient temperature, the air humidity, solar radiation and wind speed are the major components which contribute towards

the rate of evaporation (Dama-Fakir, Wurster and Toerien, 2012) .The rate of evaporation varies depending on the geographical location and other factors which plays an important role in the whole process of evaporation. These factors are discussed below.

2.9.1 **Water quality**

When soluble solids are present in the water, the vapor pressure at a particular temperature tend to be lower compared to the pure water at the same temperature, and thus the evaporation rate decreases with the increase of specific gravity of the solutions. Hence, the vapor pressure of sea water with 35,000 mg/L dissolved salts is about 2 per cent less than that of pure water at the same temperature (Finch and Hall, 2001).

2.9.2 **Water depth**

The effect of the water depth on the seasonal distribution of evaporation can be considerable because of the heat storage capacity of the water body which is, determined to a large extent by its depth.

2.9.3 **Water Vapour**

To have a better understanding of evaporation, it is imperative to have a better understanding of the vapor pressure of a liquid. The average rate of movement of the molecules of a liquid depends on the kinetic energy of the system, which is measured as temperature indirectly (Bent, 2017). The molecules of a particular liquid must have a certain characteristic minimum energy to leave the surface of the liquid (e.g., water) therefore, the molecules with greater kinetic energy will move away from the attraction of the other molecules into the ambient gas or air, as it mostly is (Coleman, 2000).

2.9.4 **Rainfall**

Rainfall is usually measured by a device known as the rain gauge. The rainfall may alter the heat content of a water body even though it may not cause significant changes and for this reason it is ignored because the volume added is generally small compared to that of the water body and so as the temperature difference.

2.10 **Meteorological factors affecting the rate of evaporation**

The estimation of evaporation of open water set-up is generally not simple because there are a number of factors that can affect the rate of evaporation, which mostly are the climate and the chemistry and physio-geography of the water body and its surroundings. Several components which have the influence on the evaporation rates are described in the following subsections.

2.10.1 **Air Temperature**

Generally, the rate of evaporation tends to increase with an increase in temperature. This is because the capacity of the air mass to hold vapor molecules increases and this is also due to increasing kinetic energy of the surface molecules which leads them to be free and become vapor. Warmer air can hold more water vapor than colder air thus, the increase of higher temperature leads to the higher rate of evaporation. Hence, it is difficult to evaporate a huge amount of moisture into the air if the water is cold. As a result, a warm air and warm water combination results into more evaporation.

2.10.2 **Water temperature**

Even at low temperatures, there are some water molecules having enough energy to escape and that's why evaporation in water can occur at any temperature (yes, even if the water is in a solid state, i.e., ice). Increase in temperature results in more molecules having kinetic energy which lead to more water evaporation.

2.10.3 **Solar radiation**

Evaporation requires a lot of energy and the primary source of energy being solar radiation. Solar radiation varies with weather conditions and the season. The incoming solar radiation warms the water body in summer and spring. During the early winter and autumn, the incoming solar radiation diminishes and thus the water body cools as the stored energy is released.

2.10.4 **Wind speed**

Generally, in nature, the incoming fresh air removes the molecules of water vapor and makes space for other vapor molecules. Obviously the faster the rates of incoming fresh air the faster the removal of vapor molecules. But once the wind velocity is sufficient to remove all rising vapor molecules extra increase in wind velocity has no effect.

In addition, the incoming fresh air if hot provides extra heat energy to accelerate process of evaporation, however if the incoming fresh air is cool it reduces the evaporation rate. One of the main functions of the wind is to remove the saturated air above the water surface during evaporation. The wind has a major influence in maintaining the atmospheric moisture gradient to allow consistent evaporation of the water. A water body exposed to a wind force greater than 2 m/s is considered to be dynamic (Marek and Straub, 2001). A higher evaporation rate can be anticipated if all other factors affecting evaporation variables work together hence the evaporation phenomena is complex. The impact from wind blowing over a water body is highly dependent on many other variables and factors. The wind speed, flow direction and wave breaking of the water, play significant roles in the rate of evaporation (Duan et al., 2009).

2.11 **Methods used for estimation of open evaporation.**

In the literature, different methods for estimating open water evaporation have been reported and they include: mass-transfer methods (Harbeck, 1962), energy budget methods (Anderson, 1954), radiation (Priestley and Taylor, 1972), combination methods (Penman, 1948), empirical methods (Kohler et al., 1954), water budget methods (Shuttleworth, 1993), and temperature based (Thornthwaite, 1948).

2.11.1 **Mass or bulk transfer balance**

This method of mass balance is simple in principle. However, the limitation of this method is that it depends on the hydrological and physio geography settings. The feasibility of determining evaporation depends primarily on the relative magnitudes of the terms. This method is not suitable to water bodies with large flows passing through since it is very difficult to obtain a reliable estimate whenever the evaporation is of the same order of magnitude as the errors inherent in the measurements. In view of the possible errors, the mass balance method is unlikely to be applicable over periods shorter than a month (Finch and Calver, 2008).

2.11.2 **Energy balance method**

Here in, the evaporation from a water body is estimated as the energy component required for closing the energy budget when all the remaining components of the budget of the water body are known, i.e. it is the residual component. Only the transfer of heat as sensible heat flux is taken into consideration , and evapotranspiration (latent heat flux) is calculated as the residual

term in the general energy balance equation (Rushdi *et al.*, 2017).The energy associated with evaporation comprises two components; the heat required to convert liquid water into water vapor (the latent heat of vaporization) and the energy of the water vapor molecules carried from (advected) the water body. The latent heat of vaporization ranges between 2.5 and 2.4 MJ/ kg for liquid water between 0 and 40°C. This method is widely considered to be the most accurate method of estimating evaporation. For this reason, is often used as a reference method against which other methods are validated or calibrated. The accuracy depends upon the size and time scale of the water body. Because of the heat storage, the larger the water body, the longer the time interval required between measurements of the temperature profile to attain acceptable accuracy in the temperature differences. The drawback of this method is that it requires many measurements, the frequency of the measurements, and the difficulties inherent in making some of them, thus making it expensive.

2.11.3 **Bulk or mass transfer**

Sene, K.J., Gash, J.H.C. and McNeil, D.D. (1991) gave a simple derivation of the bulk equation

$$E = Cu(e_s^* - e) \qquad (2.1)$$

Where C is the mass transfer coefficient, u is the wind speed and e_s * and e are the saturated vapor pressure of the air at the water surface temperature and the vapor pressure of the air at the reference height.

The transfer characteristics of the particular water body which are determined by its plant or forest cover, geometry, and the topography, climate of the surrounding land and the land use are reflected by the value of the mass transfer coefficient, C. Moreover, the value of the coefficient is specific for the characteristics of the site used to record the meteorological data; e.g. a value derived for wind speed measured at 2 m will not be correct for use with wind speed measured at 10 m, even at the same site.

Once a value for the mass transfer coefficient, C has been determined, this method requires routine measurements of wind speed and vapor pressure at the same height as the measurements used in the determination of the mass transfer coefficient ,C. Unless the water body is less than a few meters across, these measurements should be made over the water so that they are a

representative of conditions prevailing over most of the water surface. In addition, to determine * e_s the average surface temperature of the water must also be measured.

When the evaporation estimates are required on hourly or daily time scales then the effects of atmospheric stability must also be considered, however, for long-term estimates these effects can usually be neglected (Stauffer, 1991).

2.11.4 **Combination equations**

The Penman (1948) and Monteith (1965) equations are also known as combination equations since they incorporate aerodynamic water vapor mass transfer and energy balance principles. These equations are used widely for evaporation estimation because they make use of readily available meteorological data (Ershadi *et al.*, 2011). Their major limitation is that they do not take the heat storage of the water body into account if driven by net radiation data. This can be remedied by carrying out periodic thermal surveys of the water body and inputting the available energy, rather than the net radiation, into the equation, however, this makes the methods site specific.

2.11.5 **The equilibrium temperature method**

The equilibrium temperature method is a relatively new method, which might explain why there are few references to it in the literature. It is an attractive method because it is physically based, uses readily available meteorological data, and takes the heat storage of the water body into account. The only major limitation is that it assumes that the water body is uniformly mixed and thus it does not consider thermal stratification.

2.11.6 **A pan measurement**

The most used instrument to measure the evaporation rate is the evaporation pan. There are number of evaporation pans in the market for standardization of evaporation measurements. (Klink, 2006) mentioned in his thesis that the floating evaporation pan had the ability to reproduce water surface temperature similar to that of lake Hartwell since the major parameters of evaporation was the water surface temperature of the lake. However, it was suggested to investigate the impact of wind speed modifications due to the floating pan and the wooden platform.

In this project, a mostly used Class A pan was employed since it has been regarded as the commonly used amongst farmers and water resource managers (Cobaner, 2013). There are several methods which exist for either estimating or measuring evaporation from free water surfaces. The use of the evaporation pans provide one of the inexpensive, simplest and most widely used methods for evaporative losses estimations (Fekih and Saighi, 2012). Since the Class A pan has been widely used by many researchers (Rotstayn, Roderick and Farquhar, 2006; J and B, 2013; Gundalia and Dholakia, 2013; Izady *et al.*, 2016; Ghorbani *et al.*, 2018) it was then employed for this project. Measurement of evaporation loss is recorded by measuring the change in the water level of the pan. Water level changes can be recorded daily. Pan evaporation is one of the most important climatic parameters in the hydrological cycle and is often applied to estimate water requirements and terrestrial evaporation.

2.12 **Application of the estimation of evaporation of open surface using different models.**

Several studies have reported that, the meteorological parameters that are commonly known to influence and affect the process of evaporation are solar radiation, temperature, relative humidity, wind speed and atmospheric pressure (Shirgure, 2016, Sajeena *et a*l., 2017) . To date, many models have been developed to estimate the evaporation in different fields of study. (Sudheer *et al*., 2002, Sivapragasam *et al*., 2009, Izady *et al*., 2016, Sajeena *et al*., 2017, Izady *et al*., 2017). Simple methods such as the one reported by Stephens and Stewart, 1963, are handicapped because they only establish a linear relationship between the variables under investigation (Ali, 2012). This method cannot be applied for modelling OPWE because this medium is normally highly non-linear thus prompting the search for models that are capable of addressing this tendency of non-linearity's in the process since wastewater cannot be directly ascertained but only estimated depending on either the energy or water budget or mass transfer approaches (Sudheer *et al*., 2002).

Another study was reported by Sudeer *et al*., 2002) for the prediction of evaporation using artificial neural network (ANN) using Class A pans. The overarching objective of their study was to assess the ANNs potential using easily available climatic data for the estimation of evaporation and they compared their results of the Godavari Delta Irrigation project, Situated at Dowleswaram in Andhra Pradesh, India with that of Stephens and Stewart model. The ANN model showed to be superior to that of linear model Stephen and Steward suggested. They also

find that ANN is best applicable in modelling the evaporation process with restricted data. This suggests that the ANN model can be incorporated and become part of the module intended for the generation of evaporation estimation data in the studies of hydrological patterns. Moreover, it can find application in other fields including the reservoir designs, as well as water budgeting of basins, where most other models may not be appropriate.

In another report, Sajeena *et al*., 2017, developed an evaporation model for their K.C.A.E.T. campus at Tavanur in Malappuram District, using ANN technique and MATLAB software. Monthly observations of meteorological parameters during the period February 2003 to January 2009 collected were used for the model development. The data was divided into three categories, pre-monsoon observations, monsoon observations and post monsoon observations and each category contained 24 observations of each parameter. The parameters considered were monthly observation of wind speed (m/s), wet bulb temperature (°C), dry bulb temperature (°C), maximum temperature (°C), minimum temperature (°C) and evaporation (mm). For the development of the model, the data was divided randomly such that 70% of the observations were placed in a training data set, 15% in a testing data set to determine the ANN models accuracy during training in order to determine when the training should stop, and the remaining 15% for validation of the developed model. They found that the wind speed had greater influence on the evaporation rate during all seasons. Wind speed, wet bulb temperature and dry bulb temperature were found to be the accurate combination for the estimation of evaporation during all the seasons with comparatively least mean squared error (MSE) and high R^2 value. They concluded that the combination the parameters mentioned above has great influence on the evaporation during all the seasons.

Recently, Izady *et al*., 2017 conducted the study to investigate the ability of gene expression programming (GEP), adaptive neuro-fuzzy inference system (ANFIS) and ANN techniques to estimate WWE as a function of variables including wastewater physicochemical characteristics for wastewater and clear water and climatic factors. Four Class-A pans were installed, one containing clear water as a control and others contained three different wastewaters from different lagoons obtained from Neishaboor municipal wastewater treatment plant in Iran. The analysis was conducted for four months and daily CWE and wastewater evaporation (TSS, EC and water temperature) of each pan were recorded daily. In total, 366 samples were obtained for

four months, from April to July 2014. For model development, measurements from the three lagoons were considered as "input samples" to the artificial intelligent models, and they used a stepwise regression method to find the best input combinations from the collected variables. 366 samples were shuffled, 70% was used for testing and the remaining 30% was used for testing. The results obtained revealed that the ANN model had an edge over the three methods, and it demonstrated a higher accuracy when compared to dimensional analysis model using the F-test statistic. There is still no consensus with regard to which model is the best because there are some researchers who advocate that ANN is the best (Deswal and Mahesh, 2008, Sajeena *et al*., 2017) while others have the opinion that ANFIS is the best (Kisi, Mansouri and Hu, 2017, Pour-Ali Baba *et al.*, 2013) and (Terzi and Kreskin, 2005 found GEP to be the best. The difference in the opinion comes from the nature of the application and the environment where these models were applied.

In the other study, researchers such as Izady *et al*., 2016 developed equations based on the Buckingham theorem (Buckingham 1914) method using dimensional analysis for estimating WWEs as a function of CWE. Using this approach, they measured electric conductivity (EC), air temperature (Ta), total suspended solids (TSS), wind speed (W), and solar radiation, wastewater temperature (Tw) using three Class A pans for the anaerobic, primary and secondary facultative lagoons. The CWE rate was found to be less than the rate of evaporation of three wastewater lagoons and the average evaporation rate for the wastewater of three lagoons were 40.5%, 27% and 8.5% higher than that of CWE for the study period of four months(April-July 2016).

2.13 **Development of a mathematical model**

The study of modelling the rate of evaporation has been reported by various researchers and these models have been applied in different fields. The overarching objective of this study was to develop a model to estimate oil-produced water evaporation (OPWE) as a function of clear water evaporation (CWE) as well as several surrounding environmental variables including TDS, TSS, TPH, TOC, oil-produced temperature (Topw), EC, COD, BOD and the climatic variables including air temperature (Ta), Wind speed (W) and solar radiation (R). Generally, OPWE is highly nonlinear in nature, thus prompting the search for models that can address this tendency. In addition, modelling the evaporation rate is important since it cannot be directly ascertained but only estimated depending on either the energy or water budget or mass transfer approaches

(Sudheer *et al*., 2002). A very powerful and general tool for use in analyzing and understanding problems in science and engineering is known as dimensional analysis. It involves a dimensional model analysis whereby a large group of variables which arise in practical problems are reduced to its simplest algebraic form. This method is a concept of similarities and functional relations, and it is presented amongst them by a criterion equation. In modelling, the aim is to reduce the number of independent variables to the simplest form and to generalize the results thereof. This method can be effective more especially if mathematical model of the investigated process is unknown. Moreover, dimensional analysis deals with the conversion of physical quantities into other various fundamental sets of measuring units, the conversion of measuring units and other procedures. Dimensional model analysis becomes a powerful tool mostly if a complete mathematical model of the investigated process is unknown.

2.14 **Buckingham π theorem**

With the aim of providing a cost-effective and acceptable solutions to attain the model to predict compliance of the OPW; dimensional analysis based on Buckingham π theorem seems to be the best method to use for model development. Dimensional analysis based on Buckingham π theorem has been implemented by different researchers (Reddy and Reddy, 2014; Izadi *et al*., 2016; Polverino *et al.*, 2019; Misic, Najdanovic-lukic and Nesic, 2010). A physical quantity may have dimensions or be dimensionless. The physical quantities may have dimensions (that is, dimensional) or dimensionless. The numerical value of the quantity depends on the measuring units of the system. Following the Buckingham π theorem, the physical quantities are expressed in International System of units (SI) then converted to its dimensions for example, the SI units of speed of light are meter per second (m/s) and it dimensions are length per time (L/T) . Since dimensional analysis is a method of reduction of complex dependence of the physical quantity to its simplest form, it is important to the select of the parameters that have an influence/effect on the experimental data being investigated. The square brackets [] are used to show the physical quantity of the system, example, if we are interested in the speed of light (m/s) then its dimensions will be written as [L/T].

The main functions of the Buckingham π theorem are as follows:

1. Select pertinent variables (n)
2. Write the function relation (for example, $y = f(q, x, z)$)
3. Select the repeating variables (dependent variables cannot be chosen as the repeating variable, the selected variables should contain all the m dimensions (M, L, T, θ and etc.) and the non dimensionless parameters were not selected as repeating parameters.)
4. Calculate the number of π terms that the physical relationship can be reduced to (n-m).
5. Write the π terms by combining the repeating variables with each of the non-repeating variables.
6. Solve the equations obtained from step 5
7. Write the functional relationship in terms of the pi terms ($\pi_1 = f(\pi_2, \pi_3, \pi_4, \ldots . etc)$

2.15 **Conclusion**

According to new reports by the WHO and UNICEF (United Nations International Children's Emergency Fund), 2.1 billion people lack access to clean water and about 4.5 billion lack safely to adequate sanitation globally. This is due to the dwindling of the sources of freshwater and also the water pollution that plays an important role in the water crisis worldwide by reducing the freshwater resources quantity available to humans and the ecosystems (Aniyikaiye *et al.*, 2019). Countries such as China, India, South Africa (and other many African counties), as well as the whole of developing and developed countries are having a shortage in the reliable and sustainable supply of freshwater (Ganoulis, 2009). There has been a rapid industrial development in South Africa in the past century and due to this development, there has been an increase in the complex toxic effluents that have been reported in the environment. Some of the chemicals and processes used by industries used to treat produced water effluent are toxic and may even lead to secondary pollution which is one of the sources of the contamination of freshwater sources. Therefore, there is a need for a development of a model to predict the compliance of the OPW using their evaporation patterns

2.16 **References**

Abass O, A., Jameel A.T. Muyubi, S. Karim, M.A.I. and Alam, M.Z. (2011) 'Removal of Oil and Grease as Emerging Pollutants of Concern (EPC) in Wastewater Stream', *IIUM Engineering Journal*, 12(4), pp. 161–169. doi: 10.31436/iiumej.v12i4.218.

Abdullah BT, S. (2016) *Removal of oil and grease from agro-food industrial effluent using serratia marcescens sa30 and its kinetic study shakila bt abdullah universiti teknologi malaysia*. Universiti Teknologi Malaysia.

Adeniji, A. O., Okoh, O. O. and Okoh, A. I. (2017) 'Analytical Methods for the Determination of the Distribution of Total Petroleum Hydrocarbons in the Water and Sediment of Aquatic Systems : A Review', *Journal of Chemistry*, pp. 13.

Adeniyi, A. A., Yusuf, K. A. and Okedeyi, O. O. (2008) 'Assessment of the exposure of two fish species to metals pollution in the Ogun river catchments, Ketu, Lagos, Nigeria', *Environmental Monitoring and Assessment*, 137(1–3), pp. 451–458. doi: 10.1007/s10661-007-9780-5.

Adewuyi, G. O. and Olowu, R. a (2012) 'Assessment of Oil and Grease , Total Petroleum Hydrocarbons and Some Heavy Metals in Surface and Groundwater Within the Vicinity of Nnpc Oil Depot in Apata , Ibadan Metropolis , Nigeria', *International Journal of Research and Reviews*, 13(October), pp. 166–174.

Agrawal, A. and Sahu, K.K. (2009). An Overview of the Recovery of Acid from Spent Acidic Solutions from Steel and Electroplating Industries. *Journal of Hazardous Materials,* 171, 61-75.

Ahmadun, F., Pendashteh, A. and Chuah, L. (2009) 'Review of technologies for oil and gas produced water treatment', *Journal of Hazardous Materials*, 170, pp. 530–551. doi: 10.1016/j.jhazmat.2009.05.044.

Ahmed, E., El-Sayed, A. M. A. and El-Saka, H. A. A. (2007) 'Equilibrium points, stability and numerical solutions of fractional-order predator-prey and rabies models', *Journal of Mathematical Analysis and Applications*, 325(1), pp. 542–553. doi: 10.1016/j.jmaa.2006.01.087.

Ahmed, O. E., Mahmoud, S. A. and Mousa, A. E. R. (2015) 'Aliphatic and Poly-Aromatic Hydrocarbons Pollution at the Drainage Basin of Suez Oil Refinery Company', *Current Science*

International, 4(1), pp. 27–44.

Al-Kaabi, M. A., Al-Ghouti, M.A. Mohammed, Y.M.A and Ahmeed,T. (2019) 'An integrated approach for produced water treatment using microemulsions modified activated carbon', *Journal of Water Process Engineering*. Elsevier, 31, pp. 1–7. doi: 10.1016/j.jwpe.2019.100830.

Ali, M. (2012) 'Modelling Pan Evaporation Using Genetic Programming. University of Tabriz Texas A and M University of Civil Engineering University of Maragheh', 8, pp. 15–36.

Aljuboury, D. A. D. A., Palaniandy, P. Abdul, A.H.B and Feroz. S (2017) 'Treatment of petroleum wastewater by conventional and new technologies - A review', *Global Nest Journal*, 19(3), pp. 439–452. doi: 10.30955/gnj.002239.

Alther, G. (2008) 'Cleaning wastewater: Removing oil from water with organoclays', *Filtration and Separation*, 45(3), pp. 22–24. doi: 10.1016/S0015-1882(08)70057-0.

Alzahrani, S. and Mohammad, A. W. (2014) 'Challenges and trends in membrane technology implementation for produced water treatment: A review', *Journal of Water Process Engineering*. Elsevier Ltd, 4, pp. 107–133. doi: 10.1016/j.jwpe.2014.09.007.

Anderson, E.R. (1954) 'Energy-Budget Studies. In: Water loss Investigations: Lake Hefner Studies'. *Technical Report*, pp. 71-119.

Aniyikaiye, T. E., Oluseyi, T. Odiyo, J.O. and Edokpayi, J.N. (2019) 'Physico-Chemical Analysis of Wastewater Discharge from Selected Paint Industries in Lagos , Nigeria', *International Journal oF Environmental Research and Public Health*, 16, pp. 1–17. doi: 10.3390/ijerph16071235.

Atekwana, E.A., Atekwana, E.A. Rowe, R.S. Werkema Jr, D.D. and Legall, F.D (2004) 'The relationship of total dissolved solids measurements to bulk electrical conductivity in an aquifer contaminated with hydrocarbon', *Journal of Applied Geophysics*, 56, pp. 281–294. doi: 10.1016/j.jappgeo.2004.08.003.

Bent, D. (2017) *A Comparison Of Brine Evaporation Rates Under Controlled Conditions In A Laboaratory*.

Butler, B. A. and Ford, R. G. (2019) 'Evaluating relationships between total dissolved solids

(TDS) and total suspended solids (TSS) in a mining-influenced watershed', *Mine Water Environ.*, 37(1), pp. 1–12. doi: 10.1007/s10230-017-0484-y.Evaluating.

Coban, O., Kuschk, P. Wells, N.S Strauch, G. and Knoeller, K. (2015) 'Microbial nitrogen transformation in constructed wetlands treating contaminated groundwater', *Environ Sci Pollut Res*, 22(3), pp. 12829–12839. doi: 10.1007/s11356-014-3575-3.

Cobaner, M. (2013). 'Reference Evapotranspiration Based on Class A Pan Evaporation Via Wavelet Regression Technique'. *Irrigation Science*., pp.119-134

Coleman, M. (2000) *Review and Discussion on the Evaporation Rate of Brines, Members.Iinet.Net.Au*. Available at: http://members.iinet.net.au/~actis/evaporation_rate_of_brines.pdf.

Commendatore, M. G., Esteves, J. L. and Colombo, J. C. (2000) 'Hydrocarbons in coastal sediments of Patagonia, Argentina: Levels and probable sources', *Marine Pollution Bulletin*, 40(11), pp. 989–998. doi: 10.1016/S0025-326X(00)00042-4.

Dama-Fakir, P., Wurster, A. and Toerien, A. (2012) *Field testing to determine the evaporation rate of brine solutions formed during the membrane treatment of mine- water*.

Department of Water Affairs. (2013) *Revision of general authorisations in terms of Section 39 of the National Water Act, 1998 (Act No. 36 of 1998), No. 665. Government Gazette No. 36820, 6 September. Department of Water Affairs, Pretoria, South Africa.*

Deswal, S. and Mahesh, P. (2008) 'Artificial neural network based modeling of evaporation losses in reservoirs', *World Academy of Science, Engineering and Technology*, 39, pp. 279–283. Available at: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.193.2639&rep=rep1&type=pdf.

Duan, Z., Martin, J.L. Mcanally, W.H. and Stockstill, R.L. (2009). 'Combined Effects of Wind and Streamflow on Gas-Liquid Transfer Rate'. *Journal of Environmental Engineering*

Duffy, C. J. (2017) 'The terrestrial hydrologic cycle: an historical sense of balance', *Wiley Interdisciplinary Reviews: Water*, 4, p. 1216. doi: 10.1002/wat2.1216.

Ershadi, A., McCabe, M.F. Evans, J.P. and Walker, J.P. (2011) 'Evaluation of Energy Balance, Combination, and Complementary schemes for estimation of evaporation', *IAHS-AISH Publication*, 344, pp. 52–56.

Fekih, M. and Saighi, M. (2012) 'Measurement and Estimation of Evaporation from Water Surfaces : Application to Dams in Arid and Semi Arid Areas in Algeria', *International Journal of Mathematical , Computational, Physical , electrical and Computer Engineering*, 6(8), pp. 905–908.

Finch, J. and Calver, A. (2008) 'Methods for the quantification of evaporation from lakes', in *Methods for the quantification of evaporation from lakes prepared*, pp. 1–23.

Finch, J. W. and Hall, R. L. (2001) *Estimation of Open Water Evaporation*.

Ganoulis, J. (2009) *Risk Analysis of Water Pollution. 2nd ed.; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2009;*

Ghorbani, M. A., Kazempour,R. Chau, K. Shamshirband, S. Ghazvinei, T.P. (2018) 'Mechanics Forecasting pan evaporation with an integrated artificial neural network quantum-behaved particle swarm optimization model : a case study in', *Engineering Applications of Computational Fluid Mechanics*, 12(1), pp. 724–737. doi: 10.1080/19942060.2018.1517052.

Government Gazette (1984) *Requirements for the Purification of Wastewater or Effluent. Gazette No 9225, Regulation No 991, 18 May*.

Gundalia, M. and Dholakia, M. (2013) 'Modelling pan evaporation using mean air temperature and mean pan evaporation relationship in middle south Saurashtra Region', *International Journal of Water Resources and Environmental Engineering Review*, 5(11), pp. 622–629. doi: 10.5897/IJWREE2013.0426.

Gupta, S. K. (2011) *Morden hydrology and Sustainable water Development*.

Harbeck, G. E. (1962) 'A practical field technique for measuring reservoir evaporation utilizing mass-transfer theory' *Geological Survey Professional Paper* 272-E. US Government Printing Office, Washington, D.C. pp. 101–105.

Huddleston, J. G., Willauer, H.D. Swatloski, R.P. Visser , A.E and Rogers , R.D (1998) *Room*

temperature ionic liquids as novel media for ' clean ' liquid – liquid extraction.

Hussain, S. Z. and Maqbool, K. (2014) 'GC-MS: Principle, Technique and its application in Food Science', *International Journal of Current Science*, 13, pp. 116–126.

Ignacio, M., Gernjak, W. and Oller, I. (2008) 'Coupled solar photo-Fenton and biological treatment for the degradation of diuron and linuron herbicides at pilot scale', *Elsevier*, 72, pp. 622–629. doi: 10.1016/j.chemosphere.2008.02.043.

Igunnu, E. T. and Chen, G. Z. (2014) 'Produced water treatment technologies', *International Journal of Low-Carbon Technologies*, 9, pp. 157–177. doi: 10.1093/ijlct/cts049.

Ilavsk, J. and Hriv, J. (2004) 'Determination of Petroleum Hydrocarbons in Water By Microextraction And Capi- Llary Gas Chromatography', *Slovak Journal of Civil Engineering*, l, pp. 13–17.

Isehunwa, S. and Onovae, S. (2011) 'Evaluation of water discharge in the Nigeria-Delta', *Journal of Engineering and Applied Sciences*, 6(8), pp. 66–72.

Iwegbue, C. M., Aganbi, E. Obi, G. Osakwe, S.A, Eguvbe, P.M. Ogala, J.E. and Martincigh, S.B. (2016) 'Aliphatic hydrocarbon profiles in sediments of the Forcados River, Niger Delta, Nigeria', *Environmental Forensics*. Taylor & Francis, 17(2), pp. 144–155. doi: 10.1080/15275922.2016.1163620.

Izady A., Abdalla, O., Sadeghi, M., Majidi, M,. Karimi, A., and Chen M., (2016). Novel Approach to Modeling Wastewater Evaporation Based on Dimensional Analysis, *Water Resources Management*. Water Resources Management, 30, pp. 2801–2814. doi: 10.1007/s11269-016-1324-8.

Jamaly, S., Giwa, A. and Hasan, S. W. (2015) 'Recent improvements in oily wastewater treatment: Progress, challenges, and future opportunities', *Journal of Environmental Sciences*, 37, pp. 15–30. doi: 10.1016/j.jes.2015.04.011.

Jensen, M. E. (2014) 'Estimating evaporation from water surfaces', pp. 1–28.

Kanu, I. and Achi, O. (2011) 'Industrial Effluents and Their Impact on Water Quality of Receiving Rivers in Nigeria', *Journal of Applied Technology in Environmental Sanitation*, 1(1),

pp. 75–86.

Kettler, R. and Papastavros, E. (2000) 'Preliminary Results of Bitumen and Whole-Rock Elemental Analyses of CRP-2/2A, Victoria Land Basin, Antarctica', *Papers in the Earth and Atmospheric Sciences*, 7(3), pp. 361–367.

Kisi, O., Mansouri, I. and Hu, J. W. (2017) 'A New Method for Evaporation Modeling: Dynamic Evolving Neural-Fuzzy Inference System', *Advances in Meteorology*, 2017. doi: 10.1155/2017/5356324.

Klink, M. (2006) *Evaporation Estimation Using a Floating Pan*.

Kohler M. A (1954) 'Lake and panevaporation.Water-loss investigations:lake Hefner studies' *technical report*. US Geol Surv Prof Pap 269, pp.127–149

Kulkarni, S. J. and Goswami, A. K. (2015) 'A Review on Wastewater Treatment for Petroleum Industries and Refineries', *International Journal of Scientific Research in Science, Engineering and Technology*, 1(3), pp. 280–283.

Kvenvolden, K. and Copper, C. (2003) 'Natural seepage of crude oil into the marine environment', pp. 140–146. doi: 10.1007/s00367-003-0135-0.

Machín-Ramírez, C., Okoh, A.I. Morales, D. Mayolo-Deloisa, Quintero, R. and Treojo-Hernandez, T.R. (2008) 'Slurry-phase biodegradation of weathered oily sludge waste', *Chemosphere*, 70(4), pp. 737–744. doi: 10.1016/j.chemosphere.2007.06.017.

Magnuson, J. J., Webster, R. A. Assel, C. J. Bowser, P. J. Dillon,J. G. Eaton, H. E. Evans, E. J. Fee, R. I. Hall, L. R. Mortsch, D. W. Schindler And F. H. Quinn (1997) 'Potential effects of climate changes on aquatic systems : laurentian great lakes and precambrian shield region', *Hydrological Processes*, 11, pp. 825–871.

Marek, R., and Straub, J. (2001). 'Analysis of the Evaporation Coefficient and the Coefficient Condensation of Water'. *International Journal of Heat and Mass Transfer*. pp.39-53.

Misic, T., Najdanovic-lukic, M. and Nesic, L. (2010) 'Dimensional analysis in physics and the Buckingham theorem', *European Journal of Physiscs*, 893(31), pp. 893–906. doi: 10.1088/0143-0807/31/4/019.

Monteith, J. (1965) '*Evaporation and the environment. In: 19th Symposium of the Society of Experimental Biology'. Cambridge: Cambridge University Press*, pp. 205-234.

Morris, J., Sellaro, R. and Sarver, E. (2015) 'Residual diesel range organics in process waters from laboratory', *Oficial publication of the Society for Mining, Metallurgy & Exploration Inc.*, pp. 67–73.

Muthukumar, A., Idayachandiran, G. Kumaresan, S. Kumar, T. A. and Balasubramanian, T. (2013) 'Petroleum Hydrocarbons (PHC) in Sediments of Three Different Ecosystems from Southeast Coast of India', *International Journal of Pharmaceutical & Biological Archives*, 4(3), pp. 543–549.

Munirasu, S., Haija, M. A. and Banat, F. (2016) 'Use of membrane technology for oil field and refinery produced water treatment - A review', *Process Safety and Environmental Protection*. Institution of Chemical Engineers, 100, pp. 183–202. doi: 10.1016/j.psep.2016.01.010.

Nationalguideline_Landbasedinfluent_Dischargecoastal (2014).

Naubi, I., Zardari, N.S. Shirazi1, S. M. Farahen, N. Ibrahim, B. and Baloo. L.(2016) 'Effectiveness of Water Quality Index for Monitoring Malaysian River Water Quality', 25(1), pp. 1–9. doi: 10.15244/pjoes/60109.

Nkwocha, A., Ekeke, I.C. Kamen, F.L. and Oghome, P.I. (2013) 'Quality Assessment of Effluent Discharges from Vegetable oil Plant', *Ethiopian Journal of Environmental Studies and Management*, 6, pp. 717–723. doi: 10.4314/ejesm.v6i6.2s.

Okparanma, R. N. and Mouazen, A. M. (2013) 'Determination of total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbon (PAH) in soils: A review of spectroscopic and nonspectroscopic techniques', *Applied Spectroscopy Reviews*, 48(6), pp. 458–486. doi: 10.1080/05704928.2012.736048.

Penman, H.L. (1948) 'Evaporation in nature'. *Report on Progress in Phys*ics 11, pp.366-388.

Pimentel, D., Houser, J. Preiss, E. White, O. Fang, H. Mesnick, L. Brasky, T. Tariche, S. Schreck, J. and Alpert, S. (1997) 'Water Resources : Agriculture , the Environment , and Society. An assessment of the status of water resources', *Bioscience*, 47(2), pp. 97–106.

Polverino, P., Bovea, G. Sorrentinoa,M. Pianesea, C. and Berettab, D. (2019) 'Advancements on scaling-up simulation of Proton Exchange Membrane Fuel Cells impedance through Buckingham Pi theorem', *Applied Energy*. Elsevier, 249, pp. 245–252. doi: 10.1016/j.apenergy.2019.04.067.

Pour-Ali Baba, A., Shiri, J. Kisi, O. Fard, A.F. Kim, S. and Amini, R. (2013) 'Estimating daily reference evapotranspiration using available and estimated climatic data by adaptive neuro-fuzzy inference system (ANFIS) and artificial neural network (ANN)', *Hydrology Research*, 44(1), p. 131. doi: 10.2166/nh.2012.074.

Priestley, C.H.B. and Taylor, R.J. (1972) 'On the assessment of surface heat flux and evaporation using large-scale parameters '. *Monthly Weather Review* 100, pp.81-92.

Rahel, F. J. and Olden, J. D. (2008) 'Assessing the Effects of Climate Change on Aquatic Invasive Species', 22(3), pp. 521–533. doi: 10.1111/j.1523-1739.2008.00950.x.

Reddy, C. M. and Quinn, J. G. (1999) 'GC-MS analysis of total petroleum hydrocarbons and polycyclic aromatic hydrocarbons in seawater samples after the North Cape oil spill', *Marine Pollution Bulletin*, 38(2), pp. 126–135. doi: 10.1016/S0025-326X(98)00106-4.

Reddy, G. M. and Reddy, V. D. (2014) 'Theoretical Investigations on Dimensional Analysis of Ball Bearing Parameters by using Buckingham Pi-Theorem', *Procedia Engineering*. Elsevier B.V., 97, pp. 1305–1311. doi: 10.1016/j.proeng.2014.12.410.

Roderick, M. L. and Farquhar, G. D. (2002) 'The Cause of Decreased Pan Evaporation over the Past 50 Years', 298, pp. 1410–1412.

Røe Utvik, T. I. (1999) 'Chemical characterisation of produced water from four offshore oil production platforms in the North Sea', *Chemosphere*, 39(15), pp. 2593–2606. doi: 10.1016/S0045-6535(99)00171-X.

Rotstayn, L. D., Roderick, M. L. and Farquhar, G. D. (2006) *A simple pan-evaporation model for analysis of climate simulations : Evaluation over Australia*. doi: 10.1029/2006GL027114.

Rushdi, A. I., Al-Shaikh, I. El-Mubarak, A.H. Alnaimi, H.A.J.A. Al-Shamary, N. Hassan, H.M and Assal, M.A. (2017) 'Characteristics and sources of anthropogenic and biogenic hydrocarbons in sediments from the coast of Qatar', *Marine Pollution Bulletin*. Elsevier, 124(1),

pp. 56–66. doi: 10.1016/j.marpolbul.2017.07.014.

Sajeena, S., Gayathry, V. A. and Sharmina, V. K. (2017) 'Estimation of Pan Evaporation Using Artificial Neural Networks – A Case Study', 6, pp. 3052–3065.

Sakari, M., Hsia, B.S. Tahir, R. Rafiq,S. Nahavandi, M.D.S. Annammala, K.V. Soon, Z.Y and Yi, A.L.J 'Estuary and Sea-associated Wetlands as Final Sink for Organic Pollutants : A Case Study in Sabah , Malaysia', *International Journal of Environment and Bioenergy*, 9(1), pp. 1–16.

Salarpour, M., Yusop, Z. Jajamezadeh, M. and Yusof, F. (2014) 'Development of generalized feed forward network for predicting annual flood (Depth) of a tropical river', *Sains Malaysiana*, 43(12), pp. 1865–1871. doi: 10.17576/jsm-2014-4312-07.

Samudro, G. and Mangkoedihardjo, S. (2014) 'Review on BOD , COD and BOD / COD ratio : a triangle zone for toxic , biodegradable and stable levels, *International Journal of Academic Research*, 2(4), pp. 235–239.

Sene, K.J., Gash, J.H.C. and McNeil, D.D. (1991) 'Evaporation from a tropical lake: comparison of theory with direct measurements', *Journal of Hydrology*. 127, pp.193-217

Shirgure, P. (2016) 'Evaporation Modeling with Artificial Neural Network - A Review Review article Evaporation modeling with artificial neural network : *A review*', 2, pp. 73–84.

Shuttleworth, W.J. (1993) Evaporation. In: Maidment, D.R., (Ed.) *Handbook of Hydrology*, New York: McGraw-Hill.

Silva, R. de C. F. S., Almeida, D.G. Rufuno, R.D. Luna, J.M. Santos, V.A. Sarubbo, V.A and Leonie, A.S.(2014) 'Applications of biosurfactants in the petroleum industry and the remediation of oil spills', *International Journal of Molecular Sciences*, 15(7), pp. 12523–12542. doi: 10.3390/ijms150712523.

Stauffer, R.E. (1991) 'Testing lake energy budget models under varying atmospheric stability conditions'. *Journal of Hydrology*. 128, pp.115-135.

Sudheer, K. P., Gosain, A.K. Mohana R.D. and Saheb, S.M. (2002) 'Modelling evaporation using an artificial neural network', *Hydrological Processes*, 16, pp. 3189–3202.

Suspes, A., Roa, S. and González, C. and Castro, H.E. (2012) 'Total Petroleum Hydrocarbons By

Gas Chromatography in Colombian Waters and Soils', *American Journal of Environmental Science*, 8(4), pp. 396–402. doi: 10.3844/ajessp.2012.396.402.

Suratman, S. (2013) 'Distribution of Total Petrogenic Hydrocarbon in Dungun River Basin , Malaysia', *Oriental Journal of Chemistry*, 29(1), pp. 77–80.

Thomas, K. V., Langford, K. Perterson, K. Smith, A.J and Tollefson, K.E. (2009) 'Effect-directed identification of naphthenic acids as important in vitro xeno-estrogens and anti-androgens in North Sea offshore produced water discharges', *Environmental Science and Technology*, 43(21), pp. 8066–8071. doi: 10.1021/es9014212.

Thornthwaite, C. W., 1948: An approach towards a rational classification of climate.*Geography Review,* **38**, pp. 55–94.

Todd, G. D., Chessin, R. L. and Colman, J. (1999) *Toxilogical Profile for Total Petroleum Hydrocarbons (TPH). Public Health*.

ToxFAQs, A. for T. S. and D. R. (1999) *Total Petroleum Hydrocarbons (Tph) Agency For Toxic Substances And Disease Registry Toxfaqs*. Available at: http://www.atsdr.cdc.gov/toxfaq.html%0Ahttps://www.atsdr.cdc.gov/toxfaqs/tfacts123.pdf.

Tran, K. T., Yu, C. and Zeng, E. Y. (1997) 'Organic Pollutants In The Coastal Environment Off San Diego , California .Petrogenic And Biogenic Sources Of Aliphatic Hydrocarbons', *Environmental Toxicology and Chemistry*, 16(2), pp. 189–195.

Trick, J., Smart, M. and Reeder, S. (2008) 'Contaminated groundwater sampling and quality control of water analyses Source', *Environmental Geochemistry*, pp. 1–20.

Varjani S, Kumar G, Rene ER (2019) 'Treatment of wastewater from petroleum industry: current practices and perspectives', *Environmental Science and Pollution Research*, pp. 1–9. doi: 10.1007/s11356-019-04725-x.

Vuglinsky, V. S. (2009) *Evaporation from open water surface and groundwater, hydrological cycle*.

Weiner, E. R. (2013) 'Aquatic Chemistry', in *Applications of Environmental Aquatic Chemistry: A Practical Guide 3rd. CRC Press; Florida*, pp. 1–79.

Weisman, W. (1998) *Analysis of Petroleum Hydrocarbons in Environmental Media*.

Whitman College (2015) '*Total Suspended Solids in Water Samples*' Available at: https://www.whitman.edu/chemistry/edusolns_software/TSSBackground.pdf.

WHO & UNICEF Joint press release 2017, 2.1 Billion People Lack Safe Drinking Water at Home, More Than Twice as Many Lacks Safe Sanitation. Available online: https://www.unicef.org/media/media_96632.html (accessed on 21 August 2019).

Yang, Y., Charles, R.B. Sadriesh, N. May, J.C. Grosso, A.V.D Lyon, R.C and Faustino, P.J. (2007) 'Validation of an in vitro method for the determination of cyanide release from ferric-hexacyanoferrate : Prussian blue', *Journal of Pharmaceutical and Biomedical Analysis*, 43, pp. 1358–1363. doi: 10.1016/j.jpba.2006.11.010.

Yang, Z., Yang, C. Wang, Z. Hellebone, B. Landriault, M. and Brown, C.E. (2011) 'Oil fingerprinting analysis using commercial solid phase extraction (SPE) cartridge and gas chromatography-mass spectrometry (GC-MS)', *Analytical Methods*, 3(3), pp. 628–635. doi: 10.1039/c0ay00715c.

Yu, L., Han, M. and He, F. (2017) 'A review of treating oily wastewater', *Arabian Journal of Chemistry*, 10, pp. S1913–S1922. doi: 10.1016/j.arabjc.2013.07.020.

CHAPTER 3 : RESEARCH METHODOLOGY

This chapter narrates the details of the samples and sampling procedures, sample preparation protocols, materials and reagents used in pursuit of the research objectives for this project as well as the experimental protocols used to generate the data that provided the results reported in this dissertation.

3.1 **Materials and methods**

3.1.1 **Chemicals and materials**

A surrogate standard of 1-chlorooctadecane (96%) was purchased from Sigma-Aldrich (Johannesburg, South Africa).The solvents used for liquid-liquid extraction (LC-MS grade ethyl acetate, LC-MS grade dichloromethane and LC-MS grade hexane), cell test kits for biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) were purchased from Merck-Millipore (Darmstadt, Germany). Sodium sulphate salt and silica gel were purchased from Sigma-Aldrich (Johannesburg, South Africa).

3.1.2 **Apparatus**

Stainless steel bailer sampler was used for sampling at the oil depot. A graduated measuring device (Figure 3.2b) was used to measure the evaporated water daily from the pans. Separating funnel was used for liquid-liquid extraction (LLE) for total petroleum hydrocarbons (TPH) analysis, A vacuum filtration unit was used in the procedures for total suspended solids (TSS).

3.1.3 **Instrumentation**

(For BOD_5) analysis, the water bath was set at 20°C and used for incubation during 5-day biological oxygen demand. A Merck-Millipore UV-VIS Spectrophotometer Pharos 300 Spectroquant® was used to assess chemical oxygen demand (COD), total organic carbon (TOC), and as well as BOD_5. The thermo reactor was used for sample digestion for the COD, BOD_5 and TOC analysis. The TurboTax instrument was used to dry the extracted TPH. GCxGC-TOF-MS was used to identify and quantify the TPH from the collected samples. Multi-parameter probe, Accsen from XS (Carpi MO, Italy) field meter was used to measure the physical parameters

including electrical conductivity (EC), total dissolved solids (TDS), clear water and oil-produced water temperatures (Tcwe) and (Topw) respectively.

3.2 **Class A evaporation pan and field deployment**

3.2.1 **Fabrication of Class A pan**

The Class A pan was constructed at the UNISA's Science Campus workshop using stainless steel and has a cylindrical shape (Figure 3.1a) The diameter of the Class A evaporation pan was 12.1 cm and height 25.4 cm. To enhance air circulation under the set-up, the pan was placed over the wooden frame 15 cm from the ground.

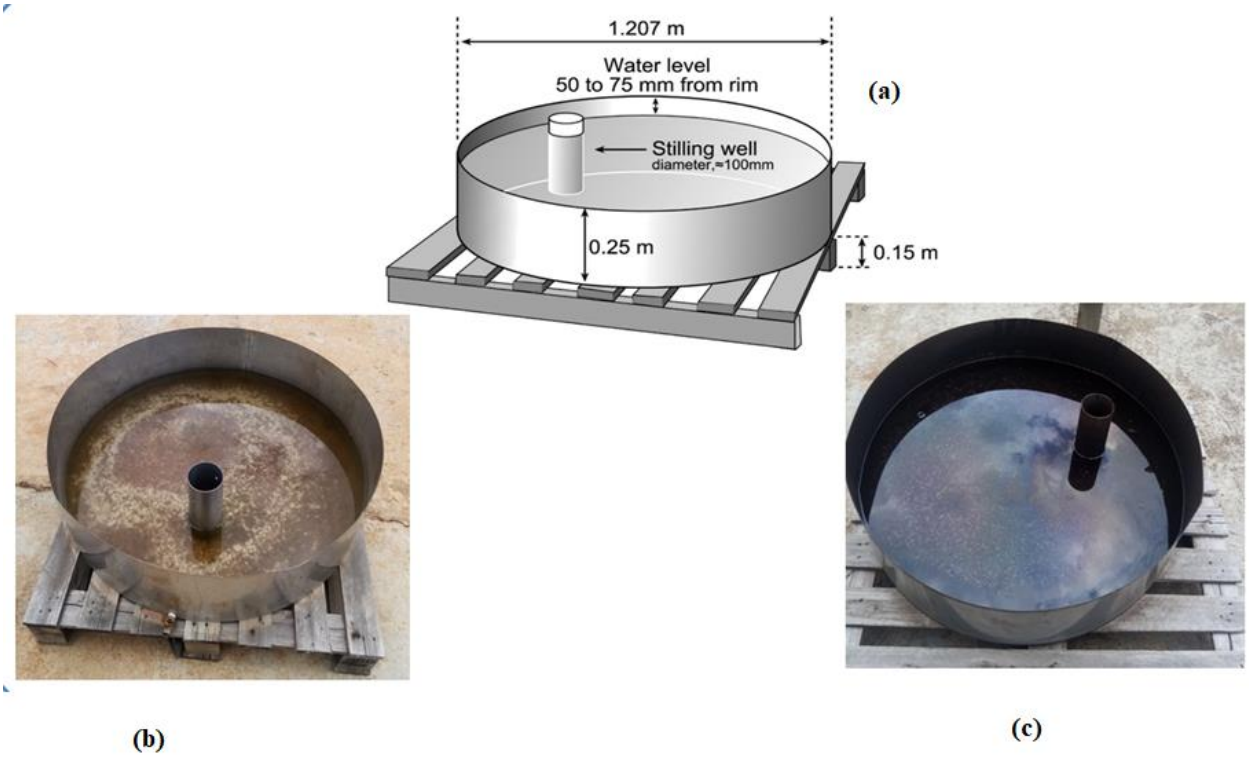

Figure 3.1: (a) Constructed evaporation pan (Izady *et al.*, 2016) (b) Class A pans filled with clear water (c) Class A pan filled with oil produced water installed at the field for this work.

3.3 **Field Measurements**

3.3.1 **Evapoartion rate measurements principle**

Two Class A pans were deployed at the field at an oil depot (Figure 3.2 a), one filled with a known volume of oil produced water (OPW) and the second was filled with the same volume of clear water. The clear water pan was meant to be the reference/control setup for measuring the evaporated water daily. The pans were installed at the site within an oil depot. The water was allowed to evaporate for 24 hours then measurements were recorded for the water depth in the pans using the water finder on the graduated measuring device (Figure 3.2 b). The difference between the two measured water depths for two successive days was then calculated by subtraction (Previous day level/depth minus today's depth/level) to give the magnitude of evapoaration Ep (in millimeter units).

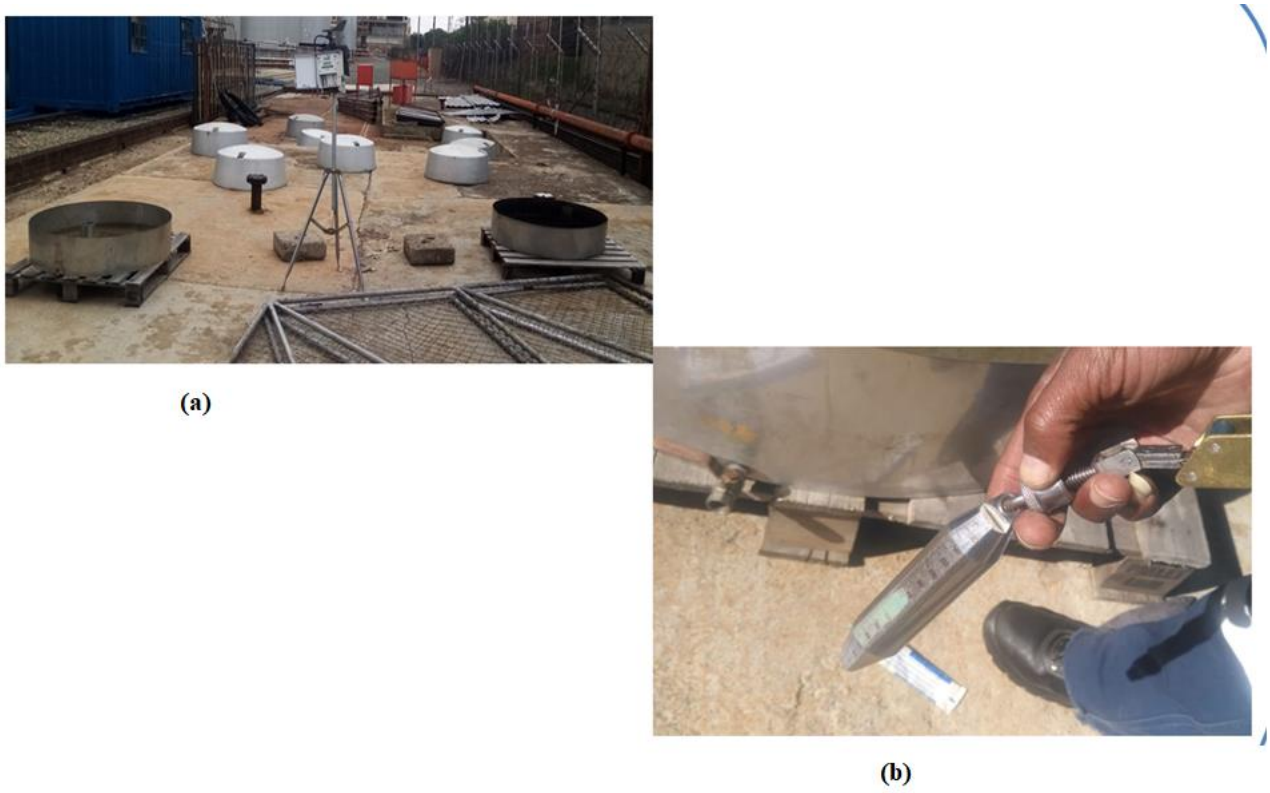

Figure 3.2: (a) Two Class A pans filled with clear water and effluent (OPW) for daily evaporation rates. (b) Measuring device and the water finder to measure the water depth.

3.3.2 **Measurements of environmental parameters in the field**

A Multi-parameter probe, Accsen from XS (Carpi MO, Italy) was permanently deployed at the field and was used for measuring water temperatures, electrical conductivities (EC) and total dissolved solids (TDS). The multimeter probe was soaked with 1% hydrochloric acid (HCl) and then rinsed with deionized water three times prior to each measurement to avoid any possibility of cross-contamination.

3.3.3 **Measurements of climatic parameters**

Climatic parameters including solar radiation (R), wind speed (W), and air temperature (Ta) were measured by a mini portable weather station (Figure 3.3) which was also deployed permanently in the field. The portable mini weather station included light intensity meter, wind vane, anemometer, temperature probe for measuring air temperature and rain gauge all in-built in the station. The rain gauge was essential in correcting the water levels during rainy days.

Figure 3.3: Portable mini-weather station installed at the oil depot.

3.4 **Description of oil depot works**

The oil depot where OPW was collected, distribute petrol, diesel, and gas to various filling stations. The influent wastewater at the depot is subjected to mechanical treatment device using skimmers to collect, contain and recover oil from the water surface. The recovered oil is temporarily stored in a built tank on a floating storage unit. After the recovery oil step, the effluent it is then discharged into the receiving water bodies. However, the oil depot effluent needs to meet the stipulated permissible limits of the local municipal. The typical schematic diagram of the oil depot works and sampling points (S) is shown in Figure 3.4

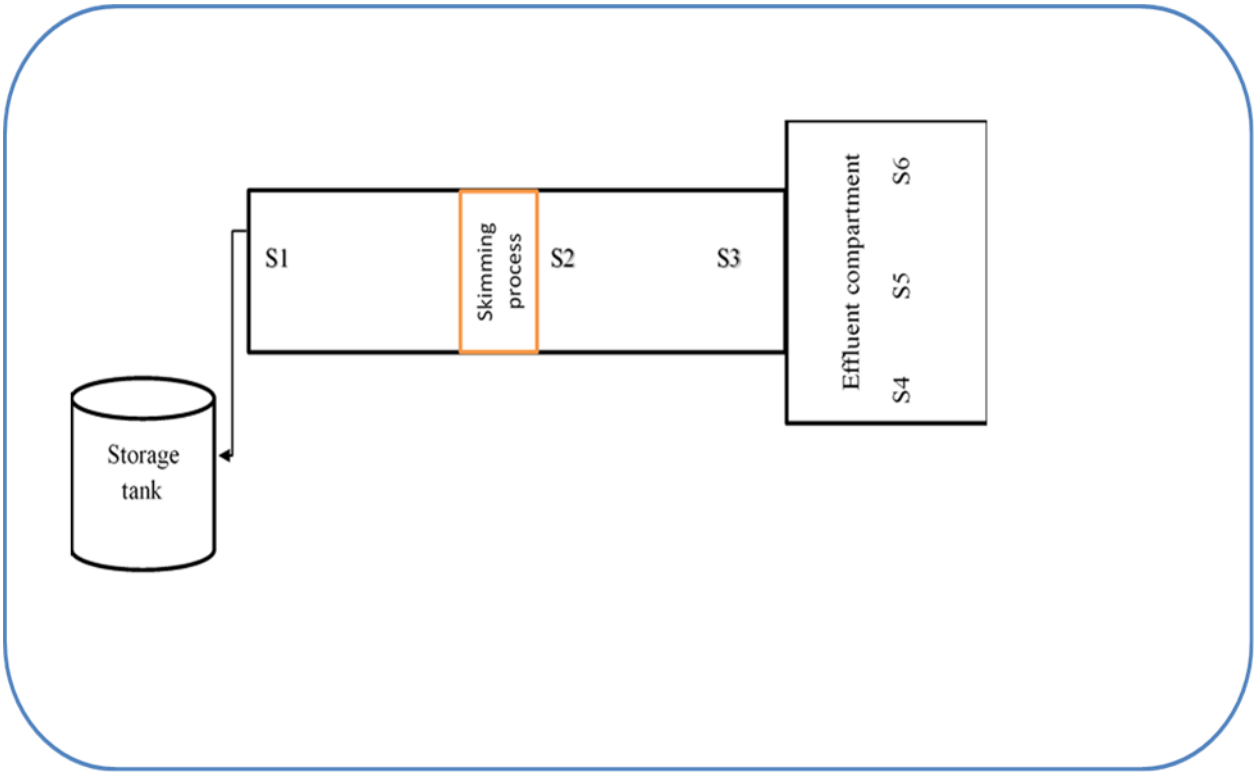

Figure 3.4: Schematic diagram of oil depot works where samples were collected**.**

Where S1 - S6 represents the sampling points.

* S (influent): 1= raw water, 2= treatment section via skimming, 3= post treated water

* S (Effluent) Discharge point: 4= (1 m apart), 5 = (1 m apart), 6=(1 m apart)

3.5 **Laboratory measurements**

3.5.1 **Sample collection and sample pre-treatment**

The water samples were collected weekly from an oil depot for the measurements of BOD, COD, TSS, TPH and TOC analysis. The sampling was conducted in a period between May and December 2019 covering all seasons (Autumn, Winter, Spring and Summer). The samples were collected at six sampling points (Figure 3.4; S1 to S6) from the influent and effluent compartments by submerging the bailer sampler device below the water surface, transferred into properly cleaned (soaked with 0.5% nitric acid for 24 hours and rinsed with deionized water prior to sampling) 1 L amber glass bottles and closed with Teflon screw caps. The bottles were rinsed with OPW (wastewater) to be collected and were then filled to overflowing, leaving no headspace, kept in the cooler box with ice and transported to UNISA laboratories located within the Science Campus in Florida Park, Roodepoort Johannesburg South Africa. The preservation of the water samples was achieved by acidifying with a few drops of 99.9% sulphuric acid to pH < 2 immediately after sampling at the field (ToxFAQs, 1999; Akporido and Onianwa, 2015; Adeniji, Okoh and Okoh, 2017). Samples were analyzed immediately upon delivery at the laboratory for TOC, COD, BOD and TSS. For TPH analysis the samples were refrigerated and analyzed within seven days. All samples were homogenized for 5 min using a vortex prior to subsampling for individual analyses.

3.6 **Spectroquant spectrophotometer instrumentation.**

The determination and quantification of COD, TOC and BOD were carried out using a Merck-Millipore UV-VIS Spectrophotometer Pharo 300 spectroquant®.

3.6.1 **BOD colorimetric method**

Normally a measure of BOD refers to the amount of dissolved oxygen needed by aerobic biological organisms to break down organic material present in a given water sample at a certain

temperature (20°C) over a specific time period (5 days) expressed in milligrams of oxygen consumed per litre of the sample. It is often used as a surrogate of the degree of organic pollution of water. BOD reduction is also used as a gauge of the effectiveness of wastewater treatment plant and also as an indication of the short-term impact on the oxygen levels of the receiving water.

3.6.1.2 **Measurements of BOD**

The BOD self-test kit purchased from Merck-Millipore (Darmstadt, Germany were used for BOD measurements using a spectroquant spectrophotometer). Following the modified Winkler method using the test kits, the pH of the samples must be kept within the range of 6-8 and the temperature of the sample including all reagents and auxiliaries must be kept within 19-21ºC. The average pH of the influent and effluent were 6.88 and 6.37 respectively and were determined using a calibrated pH meter available in the laboratory. The samples were kept at room temperature for a certain period to allow them to reach the targeted temperature. The temperature measurements were recorded using a thermometer and confirmed by the Hanna multimeter available in the laboratory. For blank determination, (BOD inoculated nutrient salt solution) was prepared by filling 0.02L of sample into 1L volumetric flask. The total contents of the vial containing the BOD nutrient salt mixture was dissolved in tap water and transferred quantitatively to the volumetric flask then filled to the mark with tap water and mixed. For the determination of both the blank and the pre-treated sample concentration, 2 glass beads were placed in each of the four oxygen bottles to avoid the formation of the bubbles. Two of the bubble free reaction bottles were filled to overflowing with pre-treated sample and the other two were filled with inoculated nutrient salt solution in the same manner. Immediately the oxygen concentration in one bottle with sample and one with nutrient salt solution were determined by adding three different ready-to-use liquid reagents in the cell test. The bubble free bottles were closed with ground glass stoppers and mixed for about 10 seconds and then. left to stand for 1 minute (reaction time). Immediately the round cells were filled with the samples and the blank to measure in the photometer (initial oxygen concentration). The other two bubble free bottles were closed with ground glass stoppers, incubated and protected from light for 5 days at 20 ºC in a water bath, and subsequently the oxygen concentration was determined as described above (

final oxygen concentration). The BOD concentrations for both blank and sample were calculated using equation 3.1 and 3.2:

$$\text{BOD}_5 \text{ of measurement sample in } (\frac{\text{mg}}{\text{L}}) = \text{measurement intial concetration} - \text{measurement final concentration} \quad (3.1)$$

$$\text{BOD}_5 \text{ of measurement balnk in}(\frac{\text{mg}}{\text{L}}) = \text{measurement intial concetration} - \text{measurement final concentration} \quad (3.2)$$

3.6.2 **Measurements of COD**

Measuring the chemical oxygen demand (COD) of wastewater is also another way of measuring the organic matter present in wastewater. The COD measurements provides a measure of the amount of oxygen consumed to chemically oxidize organic water contaminants to inorganic end products. The chemical oxygen demand test employs strong oxidizing agents to fully oxidize almost any organic compound present in the water sample to carbon dioxide.

In this work, the measure of COD just as the case for BOD was meant to be used in the model development for the estimations of the compliance to the OPW guidelines and also for fingerprinting purposes since each wastewater has characteristic measure of COD.

3.6.2.2 **COD measurements by a colometric method**

There are different methods that are used to determine COD however, in this work, colometric method based on spectrophotometric measurements was employed. The chloride content was checked with the Mquant Chloride Test and it was found to be 1084 mg/L Cl^-. This measurement was necessary because samples containing more than 2000 mg/l CL^- must be diluted with distilled water prior to determining the COD. A fixed volume of pre-treat samples (0.002L) was added, carefully allowed to run from the pipette down inside of the tilted COD reaction cell into the reagent. It was vigorously shaken to mix all the content in the reaction cell and heated in the preheated thermo reactor for 120 min at 148 ºC. The prepared blank sample was measured same way as per measurement of the sample, but with water for chromasolv (LC-MS) grade instead of the sample, this was done to increase the accuracy of the measurements. The reaction cells were

then removed, swirled after 10 min, and then allowed to cool in the test tube rack at room temperature for 30 min. The COD concentrations were measured in the spectroquant spectrophotometer (Figures 3.5)

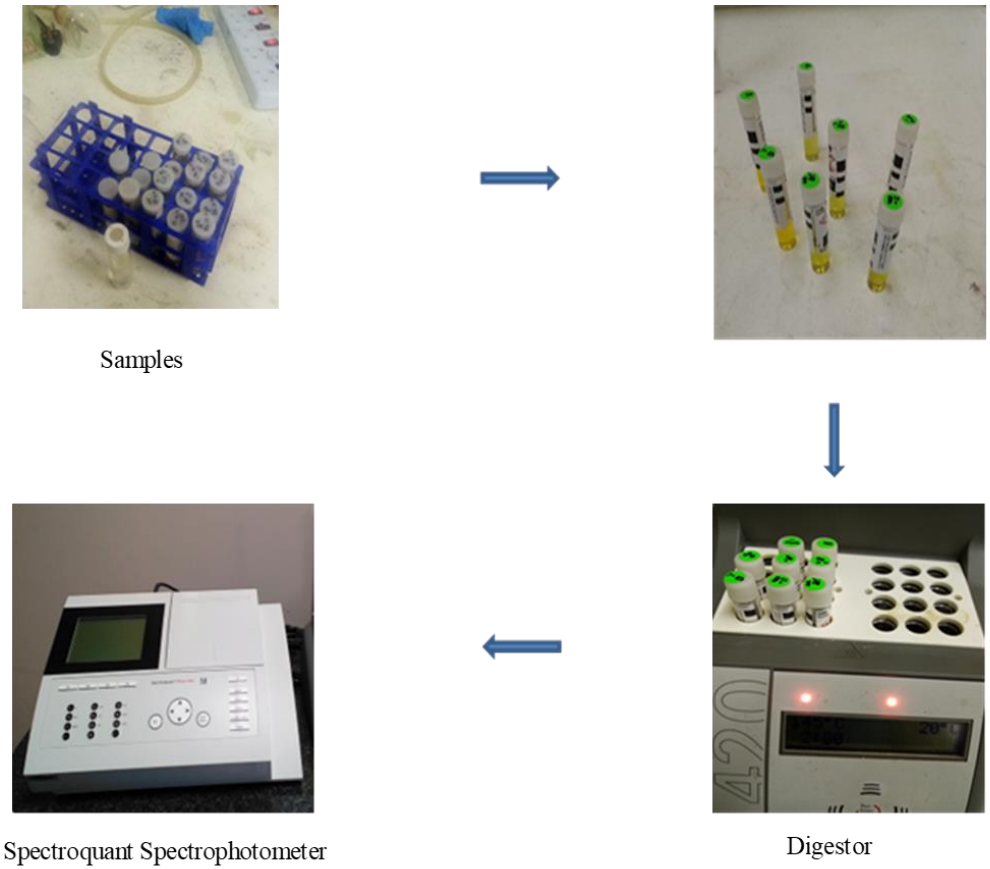

Figure 3.5: Graphical presentation of the analysis of BOD, COD and TOC using the spectroquant. (Photographed by LE Monatisa).

3.6.3 **TOC measurements**

Generally, TOC provides the organic matter present in the water sample of a given volume. TOC is a wastewater content of carbon bound in organic molecules. Organic carbon comprises nearly all carbon compounds except a few carbon species which are looked at as inorganic (carbon dioxide, carbonate, cyanide hydrogen carbonate, and some further examples which are not commonly found in wastewaters).

3.6.3.1 **Measurements of TOC**

In the measurements of TOC of the samples, a known volume (0.001L) of the sample was added to 0.009L of CHROMASOLV LC–MS grade water, stirred for 10 minutes at medium speed after adding the TOC reagents coming with the test kit. The pH was adjusted using a few drops of 96% H_2SO_4. This was necessary because the measurement of TOC for samples requires that, the pH should be below 2.5. The measured volume (0.003L) of the stirred sample was then pipetted into the reaction cell and reagent TOC-2k from the test kit was also added in the reaction cell. Immediately the cells were heated standing on their head in the preheated thermo reactor at 120 ºC for 120 min. To increase the measurement accuracy, the prepared blank was measured same way as for the sample, but with chromasolv LC–MS grade water. The reaction cells were then removed, allowed to cool in the test tube racks for 60 min. The TOC concentrations were measured in the photometer using the Spectroquant Spectrometer.

3.6.4 **Total suspended solids (TSS)**

TSS refers to the dry-weight of suspended particles, that are not dissolved, in a sample of water and that can be trapped by filter using a filtration apparatus. It is a water quality parameter that is used to assess the quality of a specimen of any type of water or water body, such as marine water or wastewater after treatment in a wastewater treatment plant.

3.6.4.1 **Measurements of total suspended solids (TSS)**

In the measurements of TSS, the laboratory reagent blank (LRB) was prepared by treating an aliquot of deionized water as a sample in all aspects. The purpose of involving LRB was to determine if the analytes or interferences are present in the laboratory environment, apparatus, or the reagents.

The analysis was done in triplicate by treating three aliquots (400 mL) of the same environmental samples identically throughout analytical procedure (Figure 3.6). The purpose was to determine precision associated with laboratory procedures (laboratory triplicate) but not with sample collection, storage, or preservation procedures.

At least one blank was measured with each analytical batch of filters (one blank for every ten samples analysed).

TSS was then calculated based on the equation 3.3

$$\text{TSS}\left(\frac{\text{mg}}{\text{L}}\right) = \left(\frac{\text{mass of the wighed filter+residue (mg)}-\text{mass o the weighed filter(mg)}}{\text{Sample volume(L)}}\right) \quad (3.3)$$

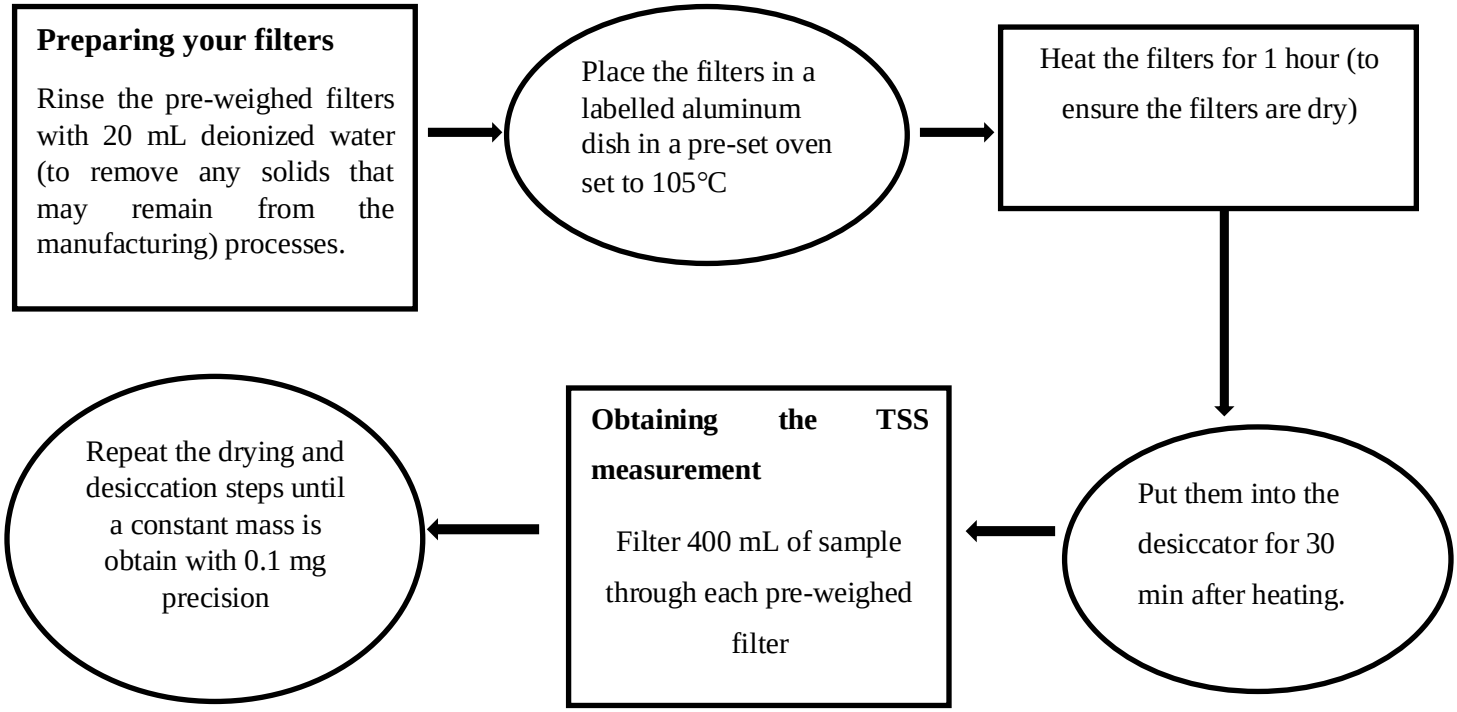

Figure 3.6: Series of procedures in the measurements of total suspended solids (TSS)

3.7 **Total petroleum hydrocarbons (TPH)**

Total petroleum hydrocarbons (TPH) is the term normally used to describe the number of petroleum-based hydrocarbons extracted and quantified by a particular method in an environmental sample matrix. The main constituents of TPHs include degraded crude oils, combusted fossil fuels, and normal alkanes compounds that are less soluble in water but are readily adsorbed onto particulate matter and are subsequently scavenged to the bottom sediment which has become a reservoir for several hydrophobic contaminants.

It is one of the parameters that is included in the guidelines for oil-produced effluents and therefore it is included in the parameters that form part of the model equation to predict the compliance to guidelines of oil-produced effluents.

3.7.1 **Sample preparation for extraction of petroleum compounds in oil-produced water**

Liquid - liquid extraction (LLE) method was developed and applied for the extraction of TPHs from OPW. Prior to LLE step, samples were filtered based on the (EPA method 3500C organic extraction and sample preparation, 2007)(Figure 3.2). Extractions were performed within 14 days after sampling. Extraction solvents that were used includes Ethyl acetate, Dichloromethane (DCM), and n-hexane, (optimization for the best solvent was done using samples from the depot). For further removal of moisture, the extracts were passed through sufficient anhydrous sodium sulphate (Na_2SO_4) with glass wool at the bottom (Figures 3.7 & 3.8). The Na_2SO_4 was purified by heating at 250°C overnight prior to the analysis.

Figure 3.7: Schematic diagram of removal of the moisture using Na_2SO_4 (Picture by LE Monatisa, 2020).

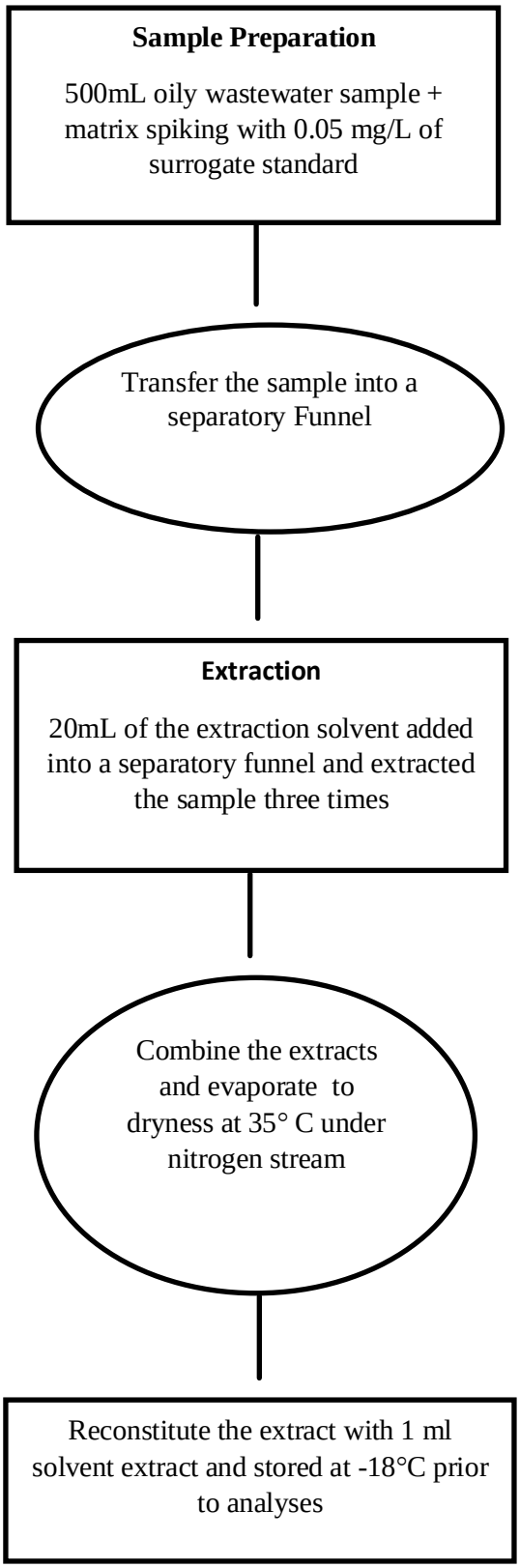

Figure 3.8: An outline of the LLE procedure used to extract TPH from OPW samples.

3.7.2 **Clean-up of LLE extracts using silica gel**

The EPA clean up method (EPA METHOD 3630C, 1996) was followed for the clean-up of OPW (LLE) extracts for TPH measurements. The extracts were cleaned up in a chromatographic column packed with the slurry prepared from 10 g activated silica gel and 2 cm Na_2SO_4 layer on top. This process was necessary in order to remove polar organic substances on the extracts prior to the TPH determination (Daniel and Nna, 2016). The samples were then eluted using 20 mL of n-pentane, concentrated and solvent exchanged to n-hexane. For quality assurance a blank sample was processed the same way. A schematic diagram of the cleaning process is shown Figure 3.9.

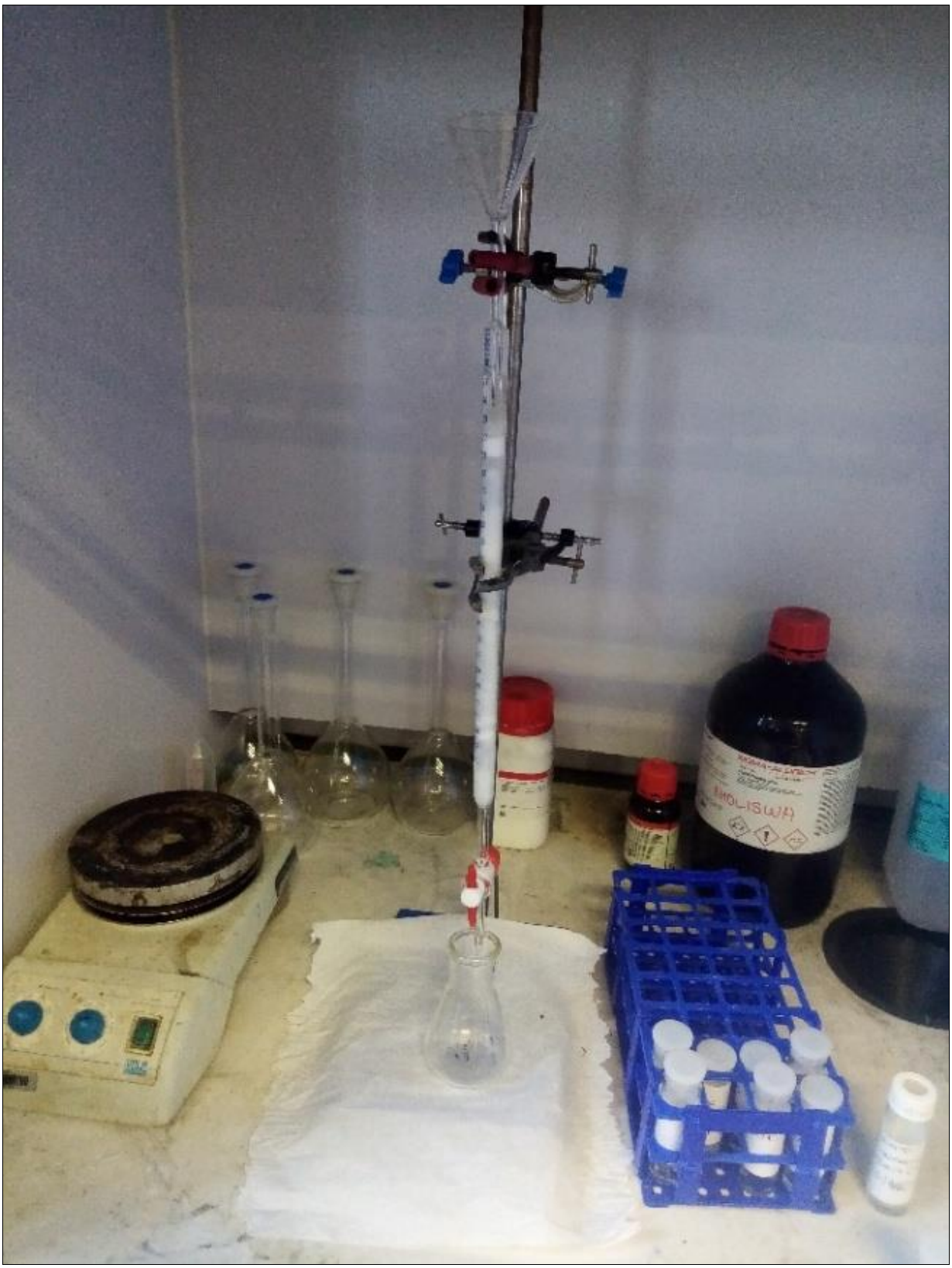

Figure 3.9: Schematic diagram of the silica gel clean-up (Picture by LE Monatisa, 2020).

3.7.3 **Preparation of standard solutions for GC x GC-TOF MS**

The primary standard stock solution was prepared by dissolving 123 µL of 99 % 1-clorooctadecane in 877 µL ethyl acetate (LC-MS grade) in a 1.5 mL amber vial and then kept at <4 ◦C till the time for analysis. The stock solution was then dissolved for 5 min under vortex (David W. Burden, 2014). From the primary stock standard solution, working calibration standard solutions of various concentrations were prepared in the range between 10 mg/L–100 mg/L for linearity, precision and recovery determinations.

3.7.4 **Measurements of TPH using GC x GC-TOF-MS**

Gas chromatography coupled with time of flight mass spectrometer (GCxGC-TOF-MS) was used for the separation and detection of the TPH extracts (analytes). DCM, ethyl acetate and n-hexane extracts of the TPHs were analysed by a LECO Pegasus 4D GCxGC-TOF-MS and helium was used as carrier gas. The analysis of samples using GCxGC-TOF-MS was performed within 40 days after the LLE extraction. The 1º GC column was Restek Rxi®-5Sil MS, 30m, 0.25mm ID, 0.25µm (Cochran, Pijpelink and Corporation, 2011). The analysis was done in a split mode using temperature programming whereby for the 1º column the initial temperature is 40ºC holding for 1 minute then ramp to 320ºC at 1.3º/min and hold for 1 minute. The initial temperature for the 2º column was 45ºC and the modulation offset temperature was 20ºC. The modulation time was 3 sec while pulse time was 1 sec. The MS data collection was performed at 1 spectra/sec.

3.8 **Model development**

3.8.1 **Establishing units of measurements in the model development**

The standard units of evaporation measurements of both the OPWE and CWE were expressed in mm/day. Evaporation rate was measured in terms of water level changes based on the differences observed between two consecutive days and expressed in mm per day (mm/day). The environmental parameters including TDS, TSS, TPH, TOC, COD and BOD were all expressed in milligram per liter (mg/L). In addition, the unit for EC of both clear water and OPW was expressed in micro Siemens per centimeter (µS/cm). The water temperature of both clear water (Tcwe) and OPW (Topw) and air temperature (Ta) were measured in degrees Celsius (°C). Other

parameters such as wind speed (W) was expressed in meter per second (m/s) whereas solar radiation (R) was measured in Lux but converted to Joules per unit time to relate the energy balance of the system.

In modeling and generation of the real experimental data, the main objective was to reduce the number of independent variables, to simplify the solution and to generalize the results thereof (Ready, GM, 2014). Following the dimensional analysis based on the Buckingham Π theorem (Buckingham, 1914), the parameters were expressed in terms of basic properties as shown in Table 3.1 i.e. their dimensions (length, mass, time and temperature).

Table 3.1: Conversion of parameters to its dimensions.

Parameters	SI units	Dimensions
OPWE	mm/day	LT^{-1}
CWE	mm/day	LT^{-1}
R	J/s	MT^{-3}
W	m/s	LT^{-1}
Ta	(°C)	Θ
Tow	(°C)	Θ
EC	μS/cm	T^{-1}
TOC	mg/L	ML^{-3}
COD	mg/L	ML^{-3}
BOD	mg/L	ML^{-3}
TPH	mg/L	ML^{-3}
TSS	mg/L	ML^{-3}
TDS	mg/L	ML^{-3}

3.9 **OPWE Equation Derivation**

The measured daily cumulative OPWE, daily cumulative CWE, OPW variables including TPH, TOC, BOD, COD, EC, TDS, TSS, and TOPW and climatic variables including W, Ta and daily cumulative solar radiation R were considered for this analysis. Dimensions of OPWE, CWE, TPH, TOC, BOD, COD, EC, TDS, TSS, TOPW, W, Ta, and R respectively were L, L, ML^{-3}, ML^{-3}, ML^{-3}, ML^{-3}, T^{-1}, ML^{-3}, ML^{-3}, θ, LT^{-1}, θ, and MT^{-2} (M: Mass, T: Time, L: Length, θ: Degree). Therefore, the number of variables was 13 and the number of basic dimensions was 4, meaning that all the variables can be combined into 9 (13 – 4) dimensionless variables (Π terms) to construct the final model.

Since the key role of the water body temperature in relation to air temperature in influencing the trend of evaporation from water bodies (Izady *et al*. 2016), this work contemplated TOPW/Ta to be one of the dimensionless variables. After an extensive search for the best model (Appendix 1), OPWE, CWE, EC, TPH, TSS, TOC, BOD and COD were regarded as the best non-repeating variables and hence TDS, W, and R were chosen as repeating variables, leading to the following dimensionless variables:

$$\begin{cases} \pi_1 = W^{a1}\, R^{b1}\, TDS^{c1}\, OPWE \\ \pi_1 = W^{a1}\, R^{b1}\, TDS^{c1}\, OPWE \\ \pi_3 = W^{a3}\, R^{b3}\, TDS^{c3}\, EC \\ \pi_4 = W^{a4}\, R^{b4}\, TDS^{c4}\, TPH \\ \pi_5 = W^{a5}\, R^{b5}\, TDS^{c5}\, TSS \\ \pi_6 = W^{a6}\, R^{b6}\, TDS^{c6}\, TOC \\ \pi_7 = W^{a7}\, R^{b7}\, TDS^{c7}\, BOD \\ \pi_8 = W^{a8}\, R^{b8}\, TDS^{c8}\, COD \end{cases} \tag{3.4}$$

where a_1, a_2, a_3, a_4, a_5, a_6, a_7, a_8, b_1, b_2, b_3, b_4, b_5, b_6, b_7, b_8, c_1, c_2, c_3, c_4, c_5, c_6, c_7, and c_8 are the powers of each variable making the Π terms dimensionless and were solved by equating the units as follows:

$$\begin{cases} (LMT\theta)^0 = (LT^{-1})^{a1}\,(MT^{-2})^{b1}\,(ML^{-3})^{c1}\,L \\ (LMT\theta)^0 = (LT^{-1})^{a2}\,(MT^{-2})^{b2}\,(ML^{-3})^{c2}\,L \\ (LMT\theta)^0 = (LT^{-1})^{a3}\,(MT^{-2})^{b3}\,(ML^{-3})^{c3}\,T^{-1} \\ (LMT\theta)^0 = (LT^{-1})^{a4}\,(MT^{-2})^{b4}\,(ML^{-3})^{c4}\,ML^{-3} \\ (LMT\theta)^0 = (LT^{-1})^{a5}\,(MT^{-2})^{b5}\,(ML^{-3})^{c5}\,ML^{-3} \\ (LMT\theta)^0 = (LT^{-1})^{a6}\,(MT^{-2})^{b6}\,(ML^{-3})^{c6}\,ML^{-3} \\ (LMT\theta)^0 = (LT^{-1})^{a7}\,(MT^{-2})^{b7}\,(ML^{-3})^{c7}\,ML^{-3} \\ (LMT\theta)^0 = (LT^{-1})^{a8}\,(MT^{-2})^{b8}\,(ML^{-3})^{c8}\,ML^{-3} \end{cases} \quad (3.5)$$

By solving Eq. (3.5) for the powers, the pi ($\pi\iota$) terms were obtained as follows:

$$\begin{cases} \pi_1 = W^2\,R^{-1}\,TDS\,OPWE \\ \pi_2 = W^2\,R^{-1}\,TDS\,CWE \\ \pi_3 = W^{-3}\,R\,TDS^{-1}\,EC \\ \pi_4 = TDS^{-1}\,TPH \\ \pi_5 = TDS^{-1}\,TSS \\ \pi_6 = TDS^{-1}\,TOC \\ \pi_7 = TDS^{-1}\,BOD \\ \pi_8 = TDS^{-1}\,COD \end{cases} \quad (3.6)$$

Considering the general form of Π terms function, Π_1 = f (Π_2, Π_3, Π_4, Π_5, Π_6, Π_7, Π_8, Π_9 = TOPW/Ta), Eq. (3.7) results in the general formulation for the OPW evaporation as follows:

$$\left(\frac{W^2\,TDS\,OPWE}{R}\right) = C\left(\frac{W^2\,TDS\,CWE}{R}\right)^{\alpha}\left(\frac{R\,EC}{W^3\,TDS}\right)^{\beta}\left(\frac{TPH}{TDS}\right)^{\gamma}\left(\frac{TSS}{TDS}\right)^{\delta}\left(\frac{TOC}{TDS}\right)^{\varepsilon}\left(\frac{BOD}{TDS}\right)^{\vartheta}\left(\frac{COD}{TDS}\right)^{\mu}\left(\frac{T_{OPW}}{T_a}\right)^{\omega} \quad (3.7)$$

A multiplicative form of the function f was applied, leading Eq. (3.8) to the final mathematical model for the OPW evaporation:

$$OPWE = \frac{C\,R}{W^2\,TDS}\left(\frac{W^2\,TDS\,CWE}{R}\right)^{\alpha}\left(\frac{R\,EC}{W^3\,TDS}\right)^{\beta}\left(\frac{TPH}{TDS}\right)^{\gamma}\left(\frac{TSS}{TDS}\right)^{\delta}\left(\frac{TOC}{TDS}\right)^{\varepsilon}\left(\frac{BOD}{TDS}\right)^{\mu}\left(\frac{COD}{TDS}\right)^{\rho}\left(\frac{T_{OPW}}{T_a}\right)^{\omega} \quad (3.8)$$

where *C*, *α*, *β*, *γ*, δ, ε, μ, ρ and ω (all dimensionless) are constants to fit the equation to the true physical relationship holding in reality and were determined using a regression analysis on the experimental data.

3.10 **Statistical analysis**

The statistical package for social sciences (IBM SPSS Statistics version 25 was used for data analysis. The analysis of variance (ANOVA) was used to determine statistically significant differences in the concentration of the OPW collected at an oil depot at a 0.05 confidence level of significance using the Microsoft excel 2016.

3.11 **Compliance study**

Department of Water affairs and water research commission (DWAF and WRC, 1995), Department of Water Affairs (DWAF) and Government Gazette, 1984 guidelines were used to assess compliance of the OPW effluents due to the prevailing environmental conditions in SA and the scope of parameters stated in the guidelines.

3.12 **References**

Adeniji, A. O., Okoh, O. O. and Okoh, A. I. (2017) 'Petroleum Hydrocarbon Profiles of Water and Sediment of Algoa Bay , Eastern Cape , South Africa', *International Journal of Environmental Research and public Health*, 10(14), pp. 1–21. doi: 10.3390/ijerph14101263.

Akporido, S. O. and Onianwa, P. C. (2015). 'Heavy Metals and Total Petroleum Hydrocarbon Concentrations in Surface Water of Esi River, Western Niger Delta'. *Research Journal of Environmental Sciences, 9: 88-100.*

Buckingham, E. (1914) 'On physically similar systems; Illustrations of the use of dimensional equations', *Physical Review*, 4(4), pp. 345–376. doi: 10.1103/PhysRev.4.345.

Cochran, J., Pijpelink, J. and Corporation, R. (2011) *GCxGC Analysis of Complex Petroleum Hydrocarbons : Sulphur Speciation in Diesel*.

Daniel, I. E. and Nna, P. J. (2016) 'Total Petroleum Hydrocarbon Concentration in Surface Water of Cross River Estuary, Niger Delta, Nigeria', *Asian Journal of Environment & Ecology*, 1(2), pp. 1–7. doi: 10.9734/ajee/2016/31102.

Department of Water Affairs. (2013) *Revision of general authorisations in terms of Section 39 of the National Water Act, 1998 (Act No. 36 of 1998), No. 665. Government Gazette No. 36820, 6 September. Department of Water Affairs, Pretoria, South Africa.*

EPA METHOD 3500C ORGANIC EXTRACTION AND SAMPLE PREPARATION (2007) *3500C - 1 Revision 3 February 2007*.

EPA METHOD 3630C (1996) *SILICA GEL CLEANUP*.

Government Gazette (1984) *Requirements for the Purification of Wastewater or Effluent. Gazette No 9225, Regulation No 991, 18 May*.

Izady A., Abdalla, O., Sadeghi, M., Majidi, M,. Karimi, A., and Chen M., (2016). Novel Approach to Modeling Wastewater Evaporation Based on Dimensional Analysis, *Water Resources Management*. Water Resources Management, 30, pp. 2801–2814. doi: 10.1007/s11269-016-1324-8.

ToxFAQs, A. for T. S. and D. R. (1999) *Total Petroleum Hydrocarbons (Tph) Agency For Toxic Substances And Disease Registry Toxfaqs*. Available at: http://www.atsdr.cdc.gov/toxfaq.html%0Ahttps://www.atsdr.cdc.gov/toxfaqs/tfacts123.pdf.

CHAPTER 4 : IDENTIFICATION OF TOTAL PETROLEUM HYDROCARBONS IN OIL PRODUCED WATER

This chapter discusses the results and observations for experiments done on the analysis of TPH in OPW samples. The TPH analysis and identification results are presented mainly qualitative with the exception of 1-chloro-octadecane, the surrogate standard. The results and discussion on the TPH compounds that were identified based on similarity index to the databases are presented and discussed in this chapter.

4.1 **Introduction**

In this chapter, an analytical method based on liquid-liquid extraction (LLE) and gas chromatography coupled to time of flight-mass spectrometry GC-TOF-MS was developed for the determination of total petroleum hydrocarbon (TPHs) in oil produced water (OPW) from an oil refinery plant. The extraction of the TPHs was achieved based on LLE technique using various extraction solvents. After the extraction the GC-MS was used to separate and identify the TPHs compounds. The extraction method involved mainly LLE after optimization of several controlling parameters followed by a cleanup process using column packed with silica gel. The GC-TOF-MS run of the extracts was then conducted. The details of the experimental procedures that were followed for TPH analysis is provided in Chapter 3 of this dissertation.

Normally contamination due to petroleum products in the environment can be identified and ascertained by determining TPHs which provides minimum information regarding the petroleum hydrocarbon present in the sample. However, certain compounds within the TPHs if present in water or edible products are known to be capable of inducing negative effects on human health (Alegbeleye, et al., 2017).

4.2 **The development and optimization of the separation and detection method for TPHs using GC-TOF-MS**

Prior to the actual extraction of analytes from environmental samples, it is desired that, the separation and detection method be developed and optimized. The choice of GC-TOF-MS as a separation and detection method, stemmed from the observation of the chemistry of the analytes which are known to be volatile and of low molecular weight. Gas chromatography (GC) is suitable for such compounds and hence the reason for the choice.

The stationary phase (GC column) used and MS conditions used are described in Chapter 3 section 3.7.

Method development used the surrogate standard (1-chloro-octadecane) which was dissolved in the appropriate solvent and injected onto the GC-TOF-MS. The signal (chromatographic peak) was observed at around 18 minutes retention time. The MS fragmentation pattern confirmed the identification of this compound.

Figure 4.1 shows the chromatograms obtained from the GC-TOF-MS run of the 1-chloro-octadecane.

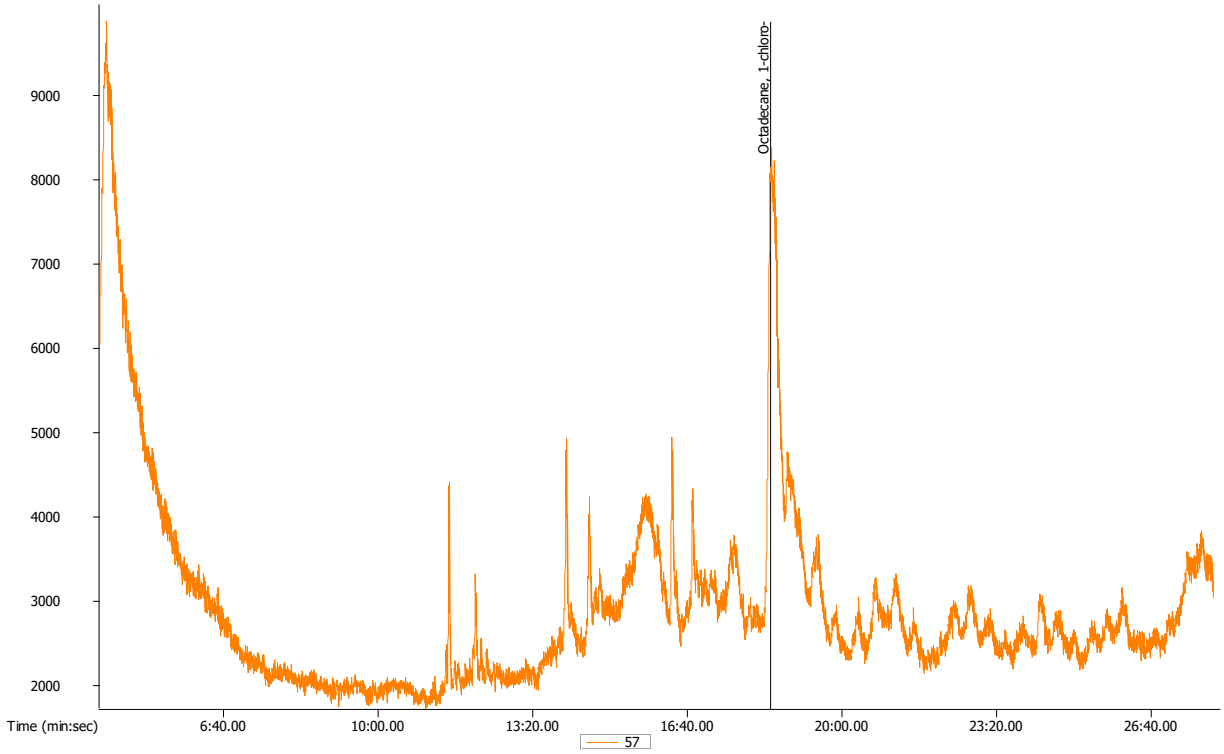

Figure 4.1a GC-MS chromatogram of standard sample, 1-chloro-octadecane

Figure 4.1a, shows the mass chromatogram of surrogate standard, 1-chloro-octadecane appeared at ~18minutes. This showed the success of the method developed and therefore it provided the means to identify the compound from OPW samples and which made the quatitation and qualitation of the compound possible. The identification of 1-chloro-octadecase was further confirmed by the mass spectral data (Figure 4.1b) where the fragmentation pattern aligned well with MS spectral pattern of the cmpound as also verified by the NIST-Library.

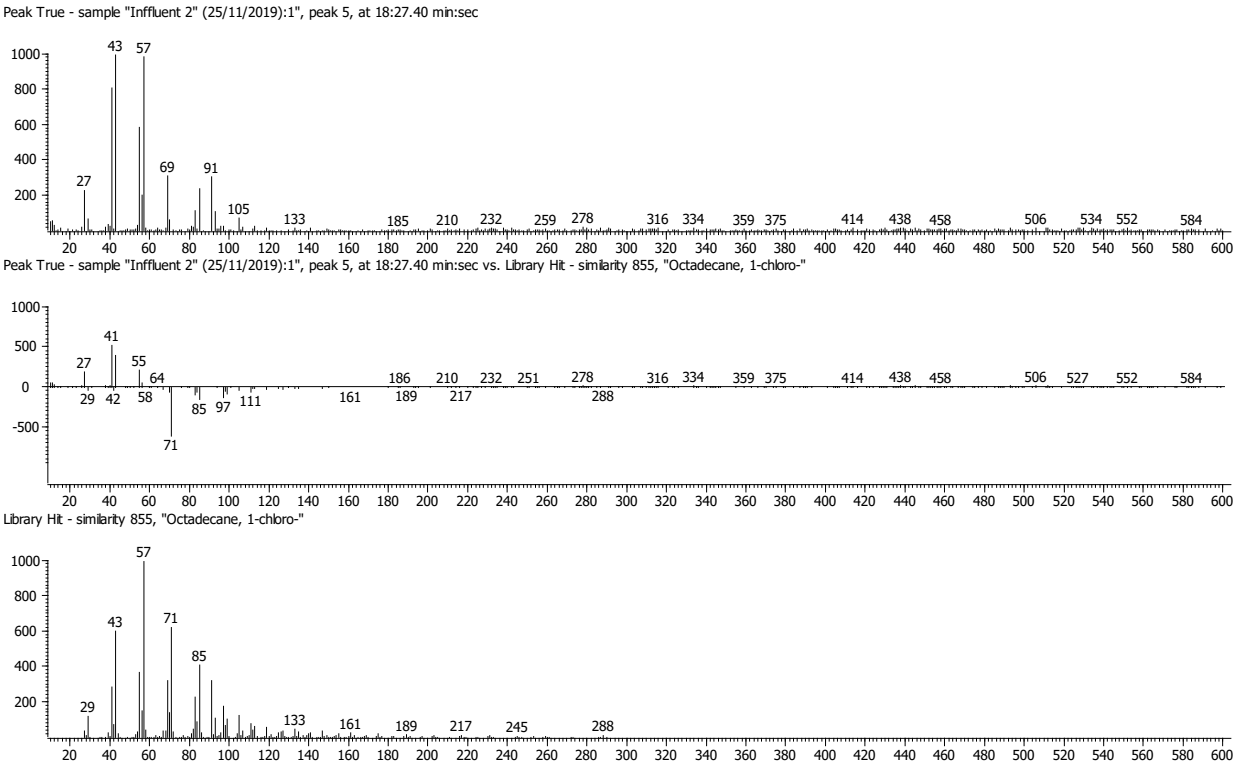

Figure 4.1b Mass spectral pattern of standard (1-chloro-octadecane)

4.3 **Liquid – Liquid Extraction (LLE) of TPHs from OPW**

In this study, LLE was selected as sample preparation method of choice for TPHs over others reported in literature simply because it is among the validated methods by EPA for TPH extraction from matrices similar to what this study dealt with.

Several organic solvents were identified and optimized for their efficiency potential to extract TPHs in OPW samples. These solvents included, n-hexane, ethyl acetate and dichloromethane (DCM). (Figure 4.2).

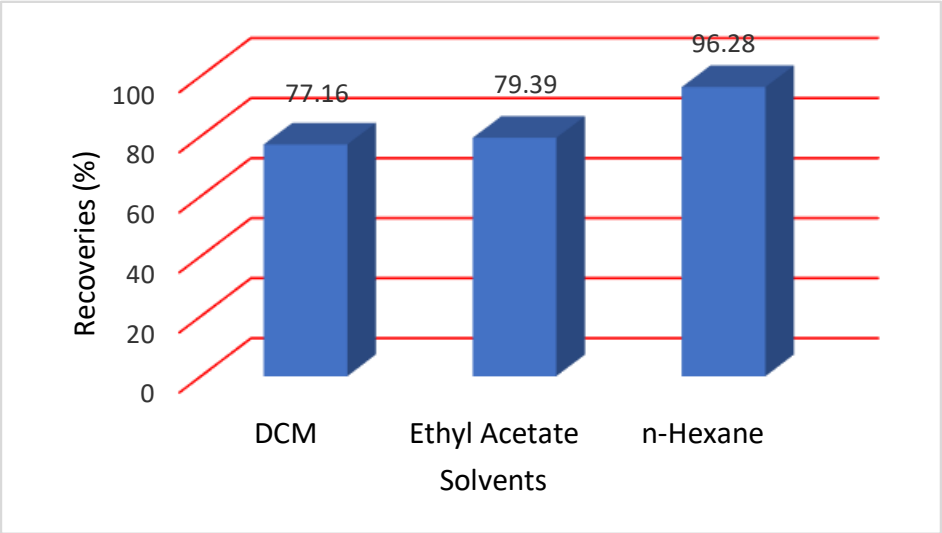

Figure 4.2: Optimization of the extraction solvents for TPH

4.3.1 **Effect of the organic phase on the extraction efficiency**

The optimization results for the organic solvents most suitable in the extraction of TPHs from OPW are presented in Figure 4.2 which clearly shows that n-hexane gave a better performance. This may be attributed to the polarity of the solvent. Of the solvent tested, n-hexane is the most non-polar and thus dissolved the compound better than other solvents. Therefore n-hexane was used in all subsequent extraction experiments for TPH from OPW samples.

4.3.2 **Optimization of organic solvent and the determination of extraction recovery efficiency**

The organic solvents that were selected and optimized included dichloromethane (DCM), ethyl acetate and n-hexane. These solvents were selected because they have low miscibility with water, and high solubility for the target analytes. The spiked deionized water was used to investigate the recovery efficiency whereby 1-chlorooctadecane was used as a surrogate indicator. The surrogate indicator was spiked into 500 mL of denoised water before extraction and concentration step. Then the spiked water was added into the separatory funnel using a measuring cylinder followed by the 20 mL of the organic sample.

The efficiency of LLE of the analytes was obtained using equation 4.1:

$$\text{Recovery}\ (\%) = \frac{C_1 - C_2}{C_3} \times 100 \quad (4.1)$$

Where C_1, C_2 and C_3 are the mean concentration of the analytes obtained. The relative standard deviation was calculated to obtain the precise extraction recovery. For quality insurance purposes, the blanks were prepared same way as the synthetic samples but without the inclusion of the surrogate standard.

The details of the experimental protocols have been given in Chapter 3 of this dissertation.

Generally, the recoveries of 1-chlorooctadecane spiked in water samples were between 77% and 96%, which is within the acceptable range of 40–140% for hydrocarbons (Adeniji, Okoh and Okoh, 2017; Kansas Department of Health and Environmental, 2015). The recoveries recorded were 96.28% for n-hexane; 77.39% for ethyl acetate and 77.16 for DCM (Figure 4.2). Therefore, n-hexane as an extracting solvent presented higher recovery as compared to other solvents. This may be attributed to its greater non-polar nature, low latent heat of vaporization (330 kJ/kg) and high selectivity to analytes as compared to other solvents (Lee, S., 2015). This is in agreement with many other researchers who have also reported on n-Hexane as being the best extract solvent particularly for TPH.

4.4 **Calibration experiments**

The quantification of the analyte in this study was performed using the external calibration curve. Linearity was demonstrated using the coefficient of liners regression (r^2) and was higher than 0.99 (Figure 4.3). The r^2 value obtained is acceptable and showed that the calibration curve can reliably be used for the quantification purposes (Agency for Toxic Substances Disease Registry, 1999). The calibration curve obtained from a plot of peak areas against concentrations of 1-chlorooctadecane that were run in the GC-TOF-MS. The 1-chlorooctadecane was found to exhibit a linear relationship for concentrations from 10mg/L to 100mg/L. This linear range is suitable as it assures that even if the concentration from the real sample is high or low, the same calibration curve will be suitable to identify and quantify the target compounds.

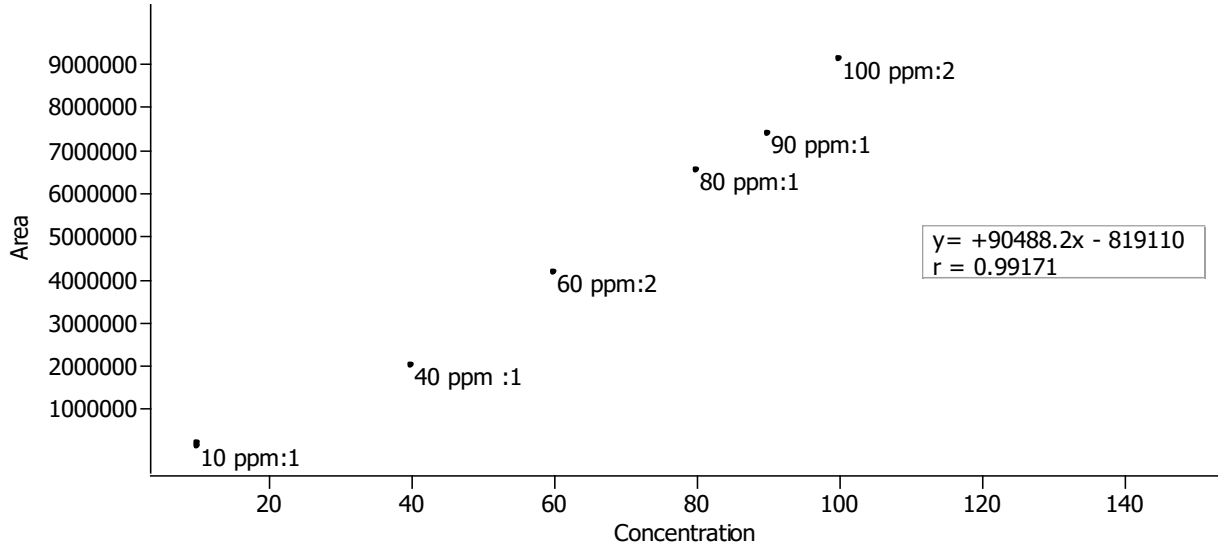

Figure 4.3: Calibration curve for 1-chlorooctadecane as a surrogate standard for THPs .

4.5 **Limit of detection and quantification determination using GC-MS.**

The limit of detection (LOD) and limit of quantification (LOQ) for TPH were estimated from the calibration curve. The working standards used for the preparation of the calibration curve were prepared from the pure analytical chemicals and they ranged from 10 mg/L to 100 mg/L. The LOD and LOQ were determined based on the signal-to noise ratio (S/N) of 3 and 10X respectivewly based on the residual standard deviation (SD) of the y-intercept of the regression line of the calibration curve and sensitivity of slope of the regression line (equations 4.2 and 4.3):

$$\mathrm{LOD} = 3.3\left(\frac{\mathrm{SD}}{\mathrm{Slope}}\right) \tag{4.2}$$

$$\mathrm{LOQ} = 10\left(\frac{\mathrm{SD}}{\mathrm{Slope}}\right) \tag{4.3}$$

To confirm the accuracy, both the LOD and LOQ were analyzed in triplicate to detect the TPHs at varying concentrations.

The LOD and LOQ of TPH using 1-chlorooactadecane surrogate standard were 100 and 355 ng/L respectively and they were obtained using GC-MS.

4.6 **Quality Control**

To ensure that the TPH measurements were a true representative of the oilfield matrix, quality control procedures to address issues including contamination, accuracy and precision of the results were conducted. All reagents and solvents used were of analytical and LCMS grades. Samples were analyzed in triplicates with blanks and spiked samples. The precision was estimated as the relative standard deviation (RSD) varied from 6.57 to 10.21% were found to be less than the maximum limit of 25% (Kansas Department of Health and Environmental, 2015; Texas Natural Resource Conservation Commission, 2001)

4.7 **Analysis of TPHs in samples collected from petroleum industry.**

After the sample preparation step, the extract was evaluated and analysed for TPHs. Various fractions were analysed including, n-alkanes, branched alkanes, alkenes, etc. by gas chromatography analysis GC-TOF-MS. The TPH compounds were characterized based on similarities between their mass spectrum and t NIST Library.

4.7.1 **Measurements of TPHs in oil produced water**

The oil produced water (OPW) from the wastewater treatment plant at an oil refinery was collected for the determination of TPH. Three samples from the influent and three from the effluent compartments were collected. After sample preparation procedures, the GC-MS was used for the determination of TPH. Samples for TPH analysis were collected weekly from May to December 2010 in a period that covered winter, autumn, spring, and summer. The study aimed at investigating the seasonal variation of TPH at the depot.

4.7.2 **GC-MS analysis of blank samples**

The analysis of the blank sample showed no presence of TPH compounds but rather other non-TPH compounds (Figures 4.4a and 4.4b).

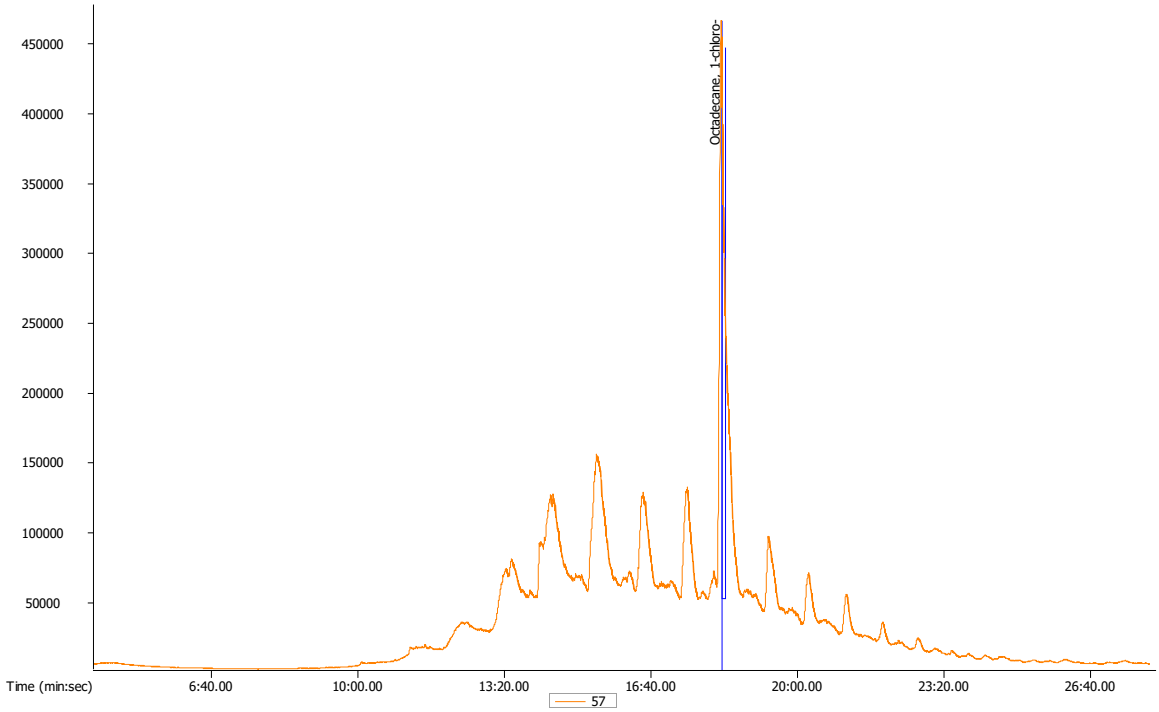

Figure 4.4a GC-MS chromatograms of the blank sample

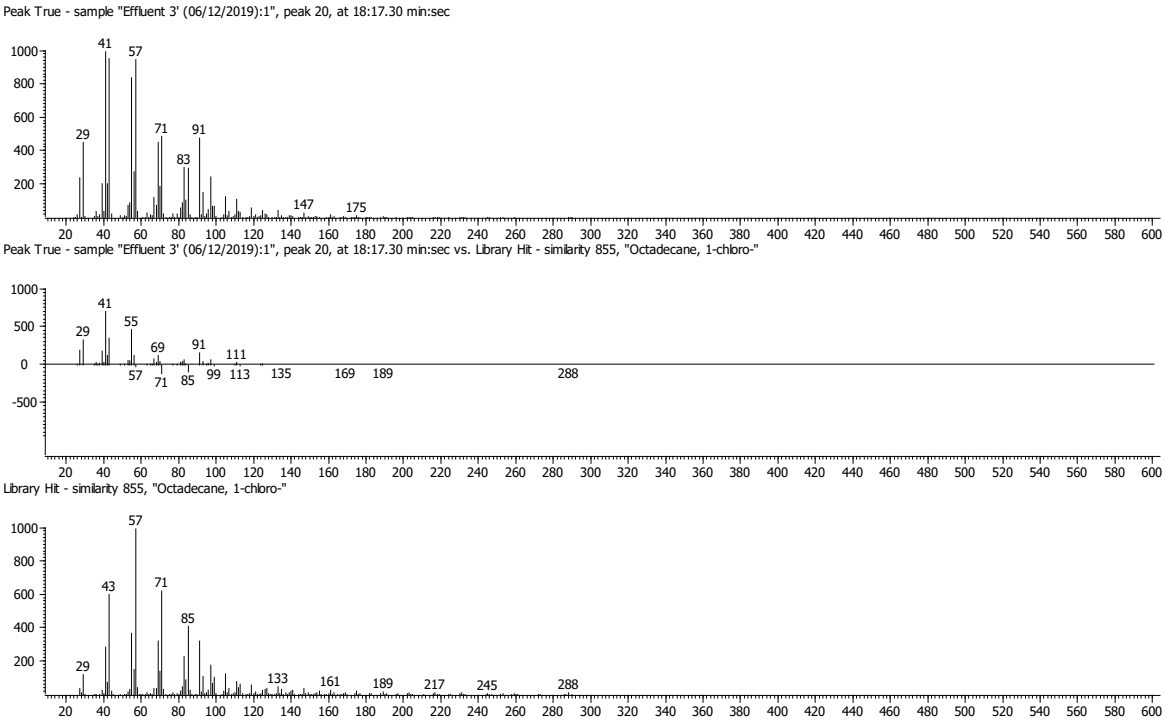

Figure 4.4b Shows the mass spectral pattern of the blank sample

4.7.3 **Alkane hydrocarbons in the influent samples in autumn 2019**

The influent samples showed the presence of different classes of TPHs including alkanes, alkenes, branched chain alkanes, branched alkenes, alkynes, cyclic aromatic hydrocarbons (Table 4.1).

Table 4.1a shows the profile of n-alkanes found in the oil produced water samples. The results showed that the influent contained more n-alkanes than the effluent. A total of 12 compounds were identified from the influent samples versus 9 that were found in the effluent samples. n-alkane hydrocarbons in the influent samples had carbon chain lengths between C 11 to C40 and of these there was a 50:50 ratio between those which are even numbered to those which are odd numbers. Compounds with carbon chain length more than 21 were more than those with less 21. The relative higher abundance of higher molecular weight alkanes signals to petroleum hydrocarbons in the matrix while the lower alkanes signals to the freshness of hydrocarbons in the environment (Tornero and d'Alcalà, 2014)

In the effluent samples, 9 compounds were identified with carbon chain lengths ranging from C14 to C36. The ratio of the even numbered alkanes to odd numbered alkanes was 55:45. The ratio of higher to lower hydrocarbons was found to be 55:45.

The measure of evenness or oddness of the alkanes provide an indication of the source of these compounds in the environment. Generally, the even numbered alkanes give an indication of the anthropogenic input while the odd numbered hydrocarbons provide an indication of the natural source of the compounds (Kachel,2008)

Table 4.1a straight chain-alkane hydrocarbons (n-alkanes) in oil produced water from an oil refinery plant for samples collected in autumn 2019

Autumn n-alkane hydrocarbons profile			
Influent		Effluent	
Name	Formula	Name	Formula
Dodecane	$C_{12}H_{26}$	Hexatriacontane	$C_{36}H_{74}$
Heneicosane	C_21H_{44}	Hexadecane	$C_{16}H_{34}$
Hentriacontane	$C_{31}H_{64}$	Nonadecane	$C_{19}H_{40}$
Heptacosane	$C_{27}H_{56}$	Octacosane	$C_{28}H_{58}$
Heptadecane	$C_{17}H_{36}$	Heptadecane	$C_{17}H_{36}$
Hexadecane	$C_{16}H_{34}$	Tetradecane	$C_{14}H_{30}$
Hexatriacontane	$C_{36}H_{74}$	Octacosane	$C_{28}H_{58}$
Nonadecane	$C_{19}H_{40}$	Heneicosane	$C_{21}H_{44}$
Octacosane	$C_{28}H_{58}$	Heptacosane	$C_{27}H_{56}$
Tetracontane	$C_{40}H_{82}$		
Tetracosane	$C_{24}H_{50}$		
Undecane	$C_{11}H_{24}$		

Table 4.1b depicts the profile of branched chain alkanes which were the dominant group of alkanes that were found in the OPW samples. A total of 24 compounds were identified from the influent samples and 16 compounds in effluent samples. The higher abundance of branched chain alkanes in the OPW can be as a result of the chemical and microbial actions that occurs while the treatment process is going on.

The observation that, effluent samples contained fewer compounds than the influent can be explained by the fact that the treatment process does remove them as well as the fact that, some may become complexed with the solid matter at the bottom.

Table 4.1b branched chain-alkane hydrocarbons in oil produced water from an oil refinery plant for samples collected in autumn 2019

Autumn TPH profile of branched chain alkane hydrocarbons			
Influent		Effluent	
Name	Formula	Name	Formula
1-Nonylcycloheptane	$C_{16}H_{32}$	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$
Benzene, [3-(2-cyclohexylethyl)-6-cyclopentylhexyl]-	$C_{25}H_{40}$	Undecane, 3,9-dimethyl-	$C_{13}H_{28}$
Bicyclo [3.1.0] hexan-2-one, 5-(1-methylethyl)-	$C_9H_{14}O$	Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$
Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$	Dodecane, 2,6,10-trimethyl-	$C1_5H_{32}$
Decane, 3,7-dimethyl-	$C_{12}H_{26}$	1-Nonylcycloheptane	$C_{16}H_{32}$
Dodecane, 1-fluoro-	$C_{12}H_{25}F$	1-Pentene, 3-ethyl-2-methyl-	C_8H_{16}
Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$	1,4-Hexadiene, 2,3,4,5-tetramethyl-	$C_{10}H_{18}$
Heptadecane, 2,6,10,14-tetramethyl-	$C_{21}H_{44}$	Pentadecane, 2,6,10-trimethyl-	$C_{18}H_{38}$
Heptyl triacontyl ether	$C_{37}H_{76}O$	4-Undecene, 10-methyl-, (E)-	$C_{12}H_{24}$
Hexanal, 4,4-dimethyl-	$C_8H_{16}O$	Undecane, 2-cyclohexyl-	$C_{17}H_{34}$
Hexane, 3,3,4,4-tetramethyl-	$C_{10}H_{22}$	Hexane, 3,3-dimethyl-	C_8H_{18}
Nonadecane, 2-methyl-	$C_{20}H_{42}$	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$
Nonane, 2,2,4,4,6,8,8-heptamethyl-	$C_{16}H_{34}$	Undecane, 2,10-dimethyl-	$C_{13}H_{28}$
Nonane, 5-methyl-	$C_{10}H_{22}$	2-Undecene, 7-methyl-	$C_{12}H_{24}$
Octadecane, 3-ethyl-5-(2-ethylbutyl)-	$C_{26}H_{54}$	Octane, 4-methyl-	C_9H_{20}
Octane, 2,6-dimethyl-	$C_{10}H_{22}$	Heptadecane, 2,6,10,14-tetramethyl-	C_21H_{44}
Octane, 4-methyl-	C_9H_{20}		
Oxetane, 3,3-dimethyl-	$C_5H_{10}O$		
Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$		
Tridecane, 6-methyl-	$C_{14}H_{30}$		
Tridecane, 7-cyclohexyl-	$C_{19}H_{38}$		
Undecane, 2,2-dimethyl-	$C_{13}H_{28}$		
Undecane, 3,5-dimethyl-	$C_{13}H_{28}$		
Undecane, 3,6-dimethyl-	$C_{13}H_{28}$		

Table 4.1c shows the profile of alkene hydrocarbons that were found in the OPW samples. The result shows that, alkene hydrocarbons were few as compared to the straight chain and branched chain alkanes. Seven (7) alkene hydrocarbon compounds were detected in the influent samples and only two (2) in the effluent samples. This can be attributed to the fact that, some chemical reactions such as photochemical reactions, action of microorganisms might be responsible for hydrogenation of enzymatic reduction of the double bonds thus making saturated compounds lose their unsaturation which resulted into fewer alkene hydrocarbons in the samples.

Table 4.1c: Alkene hydrocarbons in oil produced water from an oil refinery plant for samples collected in autumn 2019

Autumn TPH profile of alkene hydrocarbons			
Influent		Effluent	
Name	Formula	Name	Formula
1,12-Tridecadiene	$C_{13}H_{24}$	Nonacos-1-ene	$C_{29}H_{58}$
17-Pentatriacontene	$C_{35}H_{70}$	17-Pentatriacontene	$C_{35}H_{70}$
3-Tetradecene, (E)-	$C_{14}H_{28}$	Heptacos-1-ene	$C_{27}H_{54}$
4-Methyl-1,3-heptadiene	C_8H_{14}		
4-Nonene, 2,3,3-trimethyl-, (Z)-	$C1_2H_{24}$		
Cyclohexane, [6-cyclopentyl-3-(3-cyclopentylpropyl) hexyl]-	$C_{25}H_{46}$		
Nonacos-1-ene	$C_{29}H_{58}$		

Cyclic alkanes were also found to be present in the oil produced samples. Table 4.1d shows the profile of these compounds with a similar pattern as already discussed for alkanes and alkenes where the influent samples contained more of these compounds (in terms of number of compounds) than the effluent. This can as well be attributed to the efficiency of the treatment process.

Table 4.1d: cyclic-alkane hydrocarbons in oil produced water from an oil refinery plant for samples collected in autumn 2019

Autumn TPH profile of cyclic hydrocarbons			
Influent		Effluent	
Name	Formula	Name	Formula
1-Nonylcycloheptane	$C_{16}H_{32}$	Cyclopentane, methyl-	C_6H_{12}
Cyclobutane, ethyl-	C_6H_{12}	Cyclooctane, butyl-	$C_{12}H_{24}$
Cyclohexane, [6-cyclopentyl-3-(3-cyclopentylpropyl) hexyl]-	$C_{25}H_{46}$	Cyclobutane, ethyl-	C_5H_{12}
Cyclohexane, [6-cyclopentyl-3-(3-cyclopentylpropyl) hexyl]-	$C_{25}H_{46}$	Cyclopropane, 1-ethyl-2-heptyl-	$C_{12}H_{24}$
Cyclohexane, 1,1,3,5-tetramethyl-, cis-	$C_{10}H_{20}$	Cyclopentane, methyl-	C_6H_{12}
Cyclohexane, 1,3,5-trimethyl-2-octadecyl-	$C_{27}H_{54}$		
Cyclooctane, 1,4-dimethyl-, cis-	$C_{10}H_{20}$		
Cyclotetradecane	$C_{14}H_{28}$		

The results also showed the presence of few alkyne hydrocarbons as Table 4.1depicts. In this table, it shows that some compounds, mainly 3-Octyne, 7-methyl-, appear in both the influent as well as the effluent. This can be an indication of incomplete treatment of such compounds.

Table 4.1d: Alkyne hydrocarbons in oil produced water from an oil refinery plant for samples collected in autumn 2019

Autumn TPH profile of alkyne hydrocarbons			
Influent		Effluent	
Name	Formula	Name	Formula
3-Octyne, 7-methyl-	C_9H_{16}	3-Octyne, 7-methyl-	C_9H_{16}
7-Octadecyne, 2-methyl-	$C_{19}H_{36}$	8-Hexadecyne	$C_{16}H_{30}$
9-Eicosyne	$C_{20}H_{38}$		
9-Eicosyne	$C_{20}H_{38}$		
Octacosyl pentyl ether	$C_{33}H_{68}O$		

Table 4.1e shown the results for the aromatic hydrocarbons. Only two compounds were observed in the influent samples and nothing from the effluent samples. The compounds that were identified are known to be toxic and their absence in the effluent sample is good news as far as the survival of the aquatic organisms is concerned.

Table 4.1e: Aromatic hydrocarbons in oil produced water from an oil refinery plant for samples collected in autumn 2019

Autumn TPH profile of aromatic hydrocarbons			
Influent		Effluent	
Name	Formula	Name	Formula
Naphthalene, decahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1S-(1à,4aà,7à,8aá)]-	$C_{15}H_{28}$		
Naphthalene, decahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1S-(1à,4aà,7à,8aá)]-	$C_{15}H_{28}$		

4.8 **Winter profile of TPHs in oil produced water samples from an oil petroleum industry**

The winter period (June-August) registered many compounds especially from the influent compartments than they were found in Autumn season. Table 4.2a shows a comparison for the influent profile of hydrocarbons.

From Table 4.2, it is evident that branched chain alkanes dominated the profile of hydrocarbons that were found in the samples for wither season. The ratio of branched chain alkanes to n-alkanes was found to be approximately 70:30. The aromatic hydrocarbons were not found and only a few alkenes and alkynes hydrocarbons.

The effluent contained very few TPH compounds. This may mean that the quality of effluent discharged from the plant in winter times is much better than other seasons

Table 4.2: TPH profile for samples collected in winter season

Influent											
n-alkane hydrocarbons	formula	Branched	Formula	Cyclics	formula	Alkenes	formula	Alkynes	formula	Aromatics	formula
Heneicosane	$C_{21}H_{44}$	Hexane, 3,3-dimethyl-	C_8H_{18}	Cyclohexane, nonadecyl-	C25H50	1-Hexacosene	$C_{26}H52$				
Heptadecane	$C_{17}H_{36}$	Hexane, 2,3,5-trimethyl-	C_9H_{20}			1,12-Tridecadiene	$C_{13}H_{24}$				
Nonadecane	$C_{19}H_{40}$	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$			5-Eicosene, (E)-	$C_{20}H_40$				
Heneicosane	$C_{21}H_{44}$	1H-Indene, octahydro-2,2,4,4,7,7-hexamethyl-, trans-	$C_{15}H_{28}$			17-Pentatriacontene	$C_{35}H_{70}$				
Tetradecane	$C_{14}H_{30}$	Cyclooctane, 1,4-dimethyl-, trans-	$C_{10}H_{20}$			1-Undecene	$C_{11}H_{22}$				
Eicosane	$C_{20}H_{42}$	Decane, 3,8-dimethyl-	$C_{12}H_{26}$			1-Nonadecene	$C_{19}H_{38}$				
Hexadecane	$C_{16}H_{34}$	2,6,10-	$C_{16}H_{34}$								

		Trimethyltridecane									
Heptadecane	$C_{17}H_{36}$	1,5-Hexadiene, 2,5-dipropyl-	$C_{12}H_{22}$								
Heptadecane	$C_{17}H_{36}$	Decane, 2,9-dimethyl-	$C_{12}H_{26}$								
Heptacosane	$C_{27}H_{56}$	trans-Calamenene	$C_{15}H_{22}$								
Eicosane	$C_{20}H_{42}$	Undecane, 4,7-dimethyl-	$C_{13}H_{28}$								
Heneicosane	$C_{21}H_{44}$	1-Decanol, 2-hexyl-	$C_{16}H_{34}O$								
Heptadecane	$C_{17}H_{36}$	Pentadecane, 2,6,10-trimethyl-	$C_{18}H_{38}$								
Heneicosane	$C_{21}H_{44}$	Cyclohexane, 1,3,5-trimethyl-2-octadecyl-	$C_{27}H_{54}$								
Hexatriacontane	$C_{36}H_{74}$	Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$								
Heptacosane	$C_{27}H_{56}$	Heptacosane, 1-chloro-	$C_{27}H_{55}Cl$								
Decane, 2,3,6-trimethyl-	$C_{13}H_{28}$	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$								
Heptacosane	$C_{27}H_{56}$	1,12-Tridecadiene	$C_{13}H_{24}$								
Octacosane	$C_{28}H_{58}$	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	$C_{26}H_{54}$								

Heptadecane	$C_{17}H_{36}$	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	$C_{26}H_{54}$								
Heptacosane	$C_{27}H_{56}$	Dodecane, 2,6,10-trimethyl-	$C1_5H_{32}$								
Pentadecane	$C_{15}H_{32}$	Heptadecane	$C_{17}H_{36}$								
Heptadecane	$C_{17}H_{36}$	Cyclohexane, 1,3,5-trimethyl-2-octadecyl-	$C_{27}H_{54}$								
Heptacosane	$C_{27}H_{56}$	cis-2-Methyl-7-octadecene	$C_{19}H_{38}$								
Hentriacontane	$_{C3}1H_{64}$	Butane, 2,3-dimethyl-2-nitro-	$C_6H_{13}NO_2$								
Heptacosane	$C_{27}H_{56}$	Pentane, 2,3-dimethyl-	C_7H_{16}								
Hexadecane	$C_{16}H_{34}$	Decane, 4-ethyl-	$C_{12}H_{26}$								
Pentadecane	$C_{15}H_{32}$	Nonane, 3,7-dimethyl-	$C_{11}H_{24}$								
Hexatriacontane	$C_{36}H_{74}$	Decane, 2,3,6-trimethyl-	$C_{13}H_{28}$								
Hexadecane	$C_{16}H_{34}$	Decane, 5-propyl-	$C_{13}H_{28}$								
Nonadecane	$C_{19}H_{40}$	Undecane, 3-methyl-	$C_{12}H_{26}$								
Pentadecane	$C_{15}H_{32}$	Tetradecane, 2,5-dimethyl-	$C_{16}H_{34}$								
Hexadecane	$C_{16}H_{34}$	Undecane, 4-ethyl-	$C_{13}H_{28}$								
Heneicosane	$C_{21}H_{44}$	Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$								

Hentriacontane	$C_{31}H_{64}$	Tridecane, 4-methyl-	$C_{14}H_{30}$								
Octadecane	$C_{18}H_{38}$	Hexane, 3,3-dimethyl-	C_8H_{18}								
Hentriacontane	$C_{31}H_{64}$	Cyclopentane, 1-butyl-2-propyl-	$C_{12}H_{24}$								
Heptadecane	$C_{17}H_{36}$	Cyclohexane, (2-ethyl-1-methylbutylidene)-	$C_{13}H_{24}$								
Heptadecane	$C_{17}H_{36}$	Undecane, 4,6-dimethyl-	$C_{13}H_{28}$								
Heptacosane	$C_{27}H_{56}$	Octane, 3,5-dimethyl-	$C_{10}H_{22}$								
Eicosane	$C_{20}H_{42}$	Decane, 2-methyl-	$C_{11}H_{24}$								
Pentadecane	$C_{15}H_{32}$	2,2,7,7-Tetramethyloctane	$C_{12}H_{26}$								
Heptacosane	$C_{27}H_{56}$	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$								
Hexatriacontane	$C_{36}H_{74}$	Octane, 2,4,6-trimethyl-	$C_{11}H_{24}$								
Heptacosane	$C_{27}H_{56}$	Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$								
Octacosane	$C_{28}H_{58}$	Undecane, 5-ethyl-	$C_{13}H_{28}$								
Undecane	$C_{11}H_{24}$	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$								
Tetradecane	$C_{14}H_{30}$	10-Methylnonadecane	$C_{20}H_{42}$								

Tridecane	$C_{13}H_{28}$	Octadecane, 6-methyl-	$C_{19}H_{40}$								
Decane	$C_{10}H_{22}$	Nonadecane, 9-methyl-	$C_{20}H_{42}$								
Tetradecane	$C_{14}H_{30}$	Methane, tricyclohexyl-	$C_{19}H_{34}$								
Nonadecane	$C_{19}H_{40}$	Decane, 2-methyl-	$C_{11}H_{24}$								
Tetradecane	C14H 30	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$								
Pentadecane	C15H 32	Hexadecane, 2,6,10,14-tetramethyl-	$C_{20}H_{42}$								
Hexadecane	$C_{16}H_{34}$	2-Methyltetracosane	$C_{25}H_{52}$								
Pentadecane	$C_{15}H_{32}$	Decane, 2,5-dimethyl-	$C_{12}H_{26}$								
Heptadecane	$C_{17}H_{36}$										
Hexadecane	$C_{16}H_{34}$	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$								
Hexatriacontane	$C_{36}H_{74}$	10-Methyl-9-nonadecene	$C_{20}H_{40}$								
Tetradecane	$C_{14}H_{30}$	2-Methyltetracosane	$C_{25}H_{52}$								
Nonadecane	$C_{19}H_{40}$	Heptadecane, 2,3-dimethyl-	$C_{19}H_{40}$								
Heptadecane	$C_{17}H_{36}$	2-Methyltetracosane	$C_{25}H_{52}$								
Heptadecane	$C_{17}H_{36}$	Decane, 4-methyl-	$C_{11}H_{24}$								
Eicosane	$C_{20}H_{42}$	2,3-Dimethyldecane	$C_{12}H_{26}$								

Eicosane	$C_{20}H_{42}$	Decane, 3-methyl-	$C_{11}H_{24}$								
Hentriacontane	$C_{31}H_{64}$	Heptane, 2,4-dimethyl-	C_9H_{20}								
Heptacosane	$C_{27}H_{56}$	Heptane, 4-ethyl-	C_9H_{20}								
Hexatriacontane	$C_{36}H_{74}$	Pentane, 2,3,3-trimethyl-	C_8H_{18}								
Heptacosane	$C_{27}H_{56}$	Heptane, 4-propyl-	$C_{10}H_{22}$								
Hexatriacontane	$C_{36}H_{74}$	Heptane, 2,5-dimethyl-	C_9H_{20}								
Nonadecane	$C_{19}H_{40}$	Octane, 2-methyl-	C_9H_{20}								
Hentriacontane	$C_{31}H_{64}$	Pentane, 2,3,3-trimethyl-	C_8H_{18}								
Nonadecane	$C_{19}H_{40}$	Octane, 2,3,6,7-tetramethyl-	$C_{12}H_{26}$								
Octacosane	C28H58	Decane, 3-methyl-	$C_{11}H_{24}$								
Hentriacontane	C31H64	Heptane, 3,3,4-trimethyl-	$C_{10}H_{22}$								
Pentadecane	C15H32	Undecane, 2,3-dimethyl-	$C_{13}H_{28}$								
Heptacosane	C27H56	Decane, 4-ethyl-	$C_{12}H_{26}$								
Octacosane	C28H	Heptane, 4-propyl-	$C_{10}H_{22}$								

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Nonadecane	C19H40	Hexane, 2,4-dimethyl-	C_8H_{18}								
Heptacosane	$C_{27}H_{56}$	Undecane, 4-methyl-	$C_{12}H_{26}$								
Hexatriacontane	$C_{36}H_{74}$	Undecane, 2-methyl-	$C_{12}H_{26}$								
		Dodecane, 4-methyl-	$C_{13}H_{28}$								
		Undecane, 3-methyl-	$C_{12}H_{26}$								
		Decane, 2,5-dimethyl-	$C_{12}H_{26}$								
		Undecane, 2-methyl-	$C_{12}H_{26}$								
		Decane, 2,3,7-trimethyl-	$C_{13}H_{28}$								
		Octadecane, 6-methyl-	$C_{19}H_{40}$								
		Undecane, 5-ethyl-	$C_{13}H_{28}$								
		Tridecane, 4-methyl-	$C_{14}H_{30}$								
		Decane, 4-methyl-	$C_{11}H_{24}$								
		Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$								
		Pentane, 2,2-dimethyl-	C_7H_{16}								
		Undecane, 2,6-dimethyl-	$C_{13}H_{28}$								
		Decane, 4-ethyl-	$C_{12}H_{26}$								
		Undecane, 3-methyl-	$C_{12}H_{26}$								

		Undecane, 3,8-dimethyl-	$C_{13}H_{28}$								
		Dodecane, 3-methyl-	$C_{13}H_{28}$								
		Undecane, 6-ethyl-	$C_{13}H_{28}$								
		Octane, 2,3,7-trimethyl-	$C_{11}H_{24}$								
		10-Methylnonadecane	$C_{20}H_{42}$								
		Undecane, 3,9-dimethyl-	$C_{13}H_{28}$								
		1,1,6,6-Tetramethylspiro[4.4]nonane	$C_{13}H_{24}$								
		Undecane, 4-ethyl-	$C_{13}H_{28}$								
		Undecane, 2,6-dimethyl-	$C_{13}H_{28}$								
		Dodecane, 5-methyl-	$C_{13}H_{28}$								
		1-Iodo-2-methylnonane	$C_{10}H_{21}I$								
		Tridecane, 4-methyl-	$C_{14}H_{30}$								
		Decane, 2-methyl-	$C_{11}H_{24}$								
		Nonane, 3-methyl-	$C_{10}H_{22}$								
		Hexane, 3-ethyl-3-methyl-	C_9H_{20}								

		6-Tridecene, 7-methyl-	$C_{14}H_{28}$								
		Hexane, 3-ethyl-3-methyl-	C_9H_{20}								
		Tridecane, 6-methyl-	$C_{14}H_{30}$								
		Pentadecane, 7-methyl-	$C_{16}H_{34}$								
		Decane, 3,8-dimethyl-	$C_{12}H_{26}$								
		Tetradecane, 6,9-dimethyl-	$C_{16}H_{34}$								
		Tetradecane, 4-methyl-	C15H32								
		1-Iodo-2-methylundecane	$C_{12}H_{25}I$								
		Dodecane, 2-methyl-	$C_{13}H_{28}$								
		Hexane, 2,4-dimethyl-	C_8H_{18}								
		Tridecane, 4-methyl-	$C_{14}H_{30}$								
		Tridecane, 3-methyl-	$C_{14}H_{30}$								
		Decane, 2,8,8-trimethyl-	$C_{13}H_{28}$								
		Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$								
		Octane, 2,4,6-trimethyl-	$C_{11}H_{24}$								

		2,4-Dimethylstyrene	$C_{10}H_{12}$								
		Heneicosane, 10-methyl-	$C_{22}H_{46}$								
		Pentane, 3-ethyl-3-methyl-	C_8H_{18}								
		Octadecane, 6-methyl-	$C_{19}H_{40}$								
		Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$								
		Nonane, 3,7-dimethyl-	$C_{11}H_{24}$								
		Octadecane, 6-methyl-	$C_{19}H_{40}$								
		Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$								
		Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$								
		Decane, 3,8-dimethyl-	$C_{12}H_{26}$								
		Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$								
		Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$								
		Heptadecane, 2,6,10,15-tetramethyl-	$C_{21}H44$								
		Undecane, 3,7-dimethyl-	$C_{13}H28$								

		1,12-Tridecadiene	$C_{13}H24$								
		Octadecane, 6-methyl-	$C_{19}H_{40}$								
		Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$								
		Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$								
		Heptadecane, 2,6,10,15-tetramethyl-	$C_{21}H_{44}$								
		Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$								
		Dodecane, 2,7,10-trimethyl-	$C_{15}H_{32}$								
		Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$								
		Hexane, 2,2,5,5-tetramethyl-	$C_{10}H_{22}$								
		Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$								
		Nonane, 2,2,4,4,6,8,8-heptamethyl-	$C_{16}H_{34}$								
		Heptadecane, 2,6-dimethyl-	$C_{19}H_{40}$								

4.8.1 **TPH Profile in Spring and Summer.**

The profile of hydrocarbons in spring and summer, showed a similar pattern to the one observed in winter but with fewer branched and n-alkane compounds than in it is the case in winter though outnumbered the ones in autumn. The number of other compounds (cyclic, alkenes, alkynes and aromatic hydrocarbons were found to be between the autumn and winter seasons.

4.9 **Conclusion**

This work has successfully developed a method for the determination of TPH in oily wastewater samples. For determination of pollution, hydrocarbons in terms of the various classes of hydrocarbons can be used to provide better estimation of their origins and mostly important the extent of the pollution from oil produced water. Moreover, the comparison of these TPH fractions can be used to indicate the freshness or ageing fractions that can be found the oily effluents. This conclusion is also supported by the ratios of various fractions of hydrocarbons which represents the measure of hydrocarbons that can contaminate the receiving water bodies such as rivers which receive wastewater from oil refinery plants. Moreover, the results have shown that, different seasons within the same annual calendar has different profiles of TPHs. This is important where the industry is to ensure compliance throughout the year. This can also guide the industry to design appropriately their treatment plants to cater for the volume of influent based on the chemical composition. This study has also differentiated the TPH compounds in the influent and effluent samples based on the origin, whether the origin is the natural environment of it is anthropogenic. This finding will be very important to the industry to fingerprint the influent/effluent streams thus differentiate any foreign/alien components that may intrude their wastewater treatment plants.

4.10 **References**

Adeniji, A. O., Okoh, O. O. and Okoh, A. I. (2017) 'Petroleum Hydrocarbon Fingerprints of Water and Sediment Samples of Buffalo River Estuary in the Eastern Cape Province , South Africa', *Journal of Analytical Methods in Chemistry*, pp. 1–13.

Alegbeleye, Oluwandara oluwaseum, Beatrice Oluwatoyin Opeolu, and Vannesa Angela Jackson. "olycyclic Aromatic hydrocarbons:A critical review of Environmental Occurrence and Biomediation." *Environmental Management*, 2017: 758-783.

Agency for Toxic Substances and Disease Registry (ATSDR) (1999). *Toxicological Profile f*or *Total Petroleum hydrocarbon*; Deepartment of Health and Human Services, PublicHealth Service: Atlanta, GA, USA. pp. 17 - 33.

Kachel M. J. (2008) *Particularly Sensitive Sea Areas: The IMO's Role in Protecting Vulnerable Marine Areas*. New York, NY, USA: Springer.

Kansas Department of Health and Envrionmental (KDHE) (2015). *Kansas Method for the Ditermination of Mid-Range Hydrocarbons(MRH) and High-Range Hydrocabons (HRH);*Kansas Department of Health and Environment: Topeka, KS, USA. pp. 18 - 20.

Lee, S., (2015) *A Study of Latent Heat of Vaporization in Aqueous Nanofluids*.Arizona State University.

Stenstrom, M.K., Fam, S. and Silverman, G.S. (1986) 'Analytical methods for quantitative and qualitative determination of hydrocarbons and oil and grease in water and wastewater' *Environmental Technology Letters*, (1-12) 7, pp. 625–636.

Syakti, A.D., (2016) ' Molecular Diagnostic Ratios To Assess The Apportionment Of Petroleum Hydrocarbons Contamination In Marine Sediment Rasio Molekul Diagnostik Untuk Pendugaan Sumber Kontaminasi Hidrokarbon Minyak Bumi Di Sediment Laut Molekul' 11 (2), pp. 208 – 219 doi: 10.20884/1.jm.2016.11.2.236 – 208.

Texas Natural Resource Conservation (TNRCC) (2001). *Total Petroleum Hydrocarbons, TNCC Method 1005,* Revision 03; TNRCC: Austin, TX, USA. pp. 26.'

Tor, A., Aydin, M. E. Çengeloglu, Y. and Özcan, S. (2005) 'Using n-Alkanes for Identification of Oils in Domestic Wastewaters' *Environmental Technology*, (11) 26, pp. 1289-1295

Tornero V., and d'Alcalà M. R (2014)'Contamination by hazardous substances in the Gulf of Naples and nearby coastal areas: a review of sources, environmental levels and potential impacts in the MSFD perspective ' *Science of the Total Environment*. 466-467, pp. 820–840. doi: 10.1016/j.scitotenv.2013.06.106.

World Health Organization (2005) *Petroleum Products in Drinking-water, Background document for development of WHO Guidelines for Drinking-water Quality, Who/Sde/Wsh/05.08/123*

CHAPTER 5 : INVESTIGATION OF PHYSICO-CHEMICAL PARAMETERS OF OIL PRODUCED WATER DISCHARGE EFFLUENT FROM A PETROLEUM INDUSTRY

This chapter reports on the results from the analysis of various physico-chemical parameters for the effluents discharged from the petroleum industry. The parameters investigated are normally included in the guideline requirements to be met for the effluent discharged from such plants.

5.1 **Introduction**

The characteristics of effluents discharged as wastewater from industries or municipal channels and treatment plants always define the efficiency of the treatment process. Rules and regulations require that each industry must treat and process their wastes before releasing them to municipal channels or to the environment. For this reason, it is imperative that the effluents from industries are analysed for their physico-chemical parameters on a routine basis.

5.1.1 **Physico-chemical parameters from petroleum industry effluents.**

A petroleum industry also known as oil industry include all activities that deal with processes of exploration, extraction, refining, transportation (usually by oil tankers and pipelines) and marketing of petroleum products. The largest volume of products from this industry are gasoline (petrol) and fuel oil. On the other hand, there are other industries such as the manufacturing industries including oil refining, chemical steel etc. which use products from the oil industry, they also contribute in the generation of the most highly toxic pollutants, including a variety of organic chemicals and heavy metals. Because of this, guidelines that regulate the quality of the effluents that comes from these industries have been enforced to ensure compliance by the discharging companies. Hence, it is important to have analytical methods in place in order to investigate the compliance of wastewater discharged from petroleum industries. The availability of analytical methods for ensuring compliance also means a lot when considering protecting the health of humans, aquatic species, as well as plants relying on the water bodies which may potentially become contaminated from petroleum products.

5.1.2 **Characteristics of petroleum wastewater**

Wastewater from a petroleum industry contains a variety of pollutants such as petroleum hydrocarbons, oil and grease, mercaptans phenol, sulfide, ammonia, and other organic compounds (Varjani *et al.*, 2019). These compounds are present in the effluents discharged from petroleum industry, which tend to be directly or indirectly harmful to the environment. Petroleum industries generate a large amount of oily waste either solid or liquid due to upstream and downstream operations (Varjani and Upasani, 2017; Varjani *et al.*, 2019). The terms upstream and downstream in oil and gas production refer to an oil or gas company's location in the supply chain. For example, upstream oil and gas production and other related operations are normally used to identify deposits, drill wells, and where recovery of raw materials from underground takes place. Upstream in petroleum industry are also often called exploration and production companies (Havard, 2013). Downstream oil and gas production is responsible for supplying consumers with petroleum products. Downstream operations are oil and gas processes that occur after the production phase and involve all other processes all the way to the point of sale.

5.2 **Assessment of Physicochemical Parameters in a Selected Oil Depot:**

The assessment of physico-chemical parameters was performed on samples from the influent as well as the treated final effluents of wastewater from a facility located in Gauteng Province of South Africa. As shown in Table 5.2.1 and 5.2.2, the samples that were collected from the influent are (S1-S3) and those collected from the effluent compartments are (S3-S6), and the samples collection covered all seasons of the year (from May to December 2019). The parameters investigated included electrical conductivity (EC), total dissolved solids (TDS), total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and total petroleum hydrocarbons (TPH). The analysis for BOD, COD, TSS, TOC and TPH was performed in triplicate at the UNISA laboratories located within the Science Campus in Florida Park, Roodepoort Johannesburg South Africa. EC and TDS were also measured from the samples obtained in Class A pans that were installed on site at the refinery plant using a multi-parameter probe, Accsen from XS (Carpi MO, Italy). The obtained

data was subjected to descriptive statistical analysis (95 % confident limit) using the excel, 2016 software in order to generate analysis of variance (ANOVA) statistical tests, mainly, range, means, and standard error. The results of the physicochemical qualities of samples from the different points are shown in Table 5.2.1 and 5.2.2 for samples that were measured on the site.

Table 5.2.1: Physical characteristics of wastewater of the oil depot.

		Pan measurements			
Parameter	Season	Clear water		Oil produced water	
		Range	Mean ±SD	Range	Mean ± SD
TDS (mg/L)	Autumn	130.00 – 172.00	158.51 ± 9.73	250.20 - 281.95	268.44 ± 11.00
	Winter	135.22 – 174.21	149.48 ± 6.43	218.65 - 289.00	247.23± 12.88
	Spring	135.00 – 206.00	156.41 ± 8.86	261.05 - 349.00	297.51 ± 11.48
	Summer	125.16 – 201.00	151.97 ± 7.39	271.00 - 335.00	288.02 ± 10.86
EC (μS/cm)	Autumn	170.00 - 300.60	277.61 ± 10.44	515.00 - 569.05	540.58± 11.01
	Winter	223.16 – 282.00	242.07 ± 12.56	512.13 - 568.00	538.84 ± 9.32
	Spring	223.00 - 364.00	349.14 ±11.70	518.00 -592.20	551.97 ± 12.77
	Summer	306.21 – 367.00	333.40 ± 9.43	538.00 -551.00	544.74 ± 7.03

5.2.1 **Total Dissolved Solids (TDS)**

A combined measure of the total organic and inorganic substances in a sample is known as total dissolved solids (TDS). The TDS measurements were recorded in the field throughout the study period and the measurements were assessed daily from the pans filled with clear water (control) and oil produced water (OPW). The OPW pan was filled with effluent taken from the discharging point and measurements were taken daily. The TDS measure recorded for the entire

study period generally ranged from 125.16 – 206.00 and 218.65 – 349.00 mg/L for clear water and OPW respectively (Table 5.2.1) and varied significantly ($P < 0.05$). High values of TDS for both clear water and OPW were observed in spring with total mean and standard deviation of 156.41 ± 8.86 and 297.51 ± 11.48 mg/L respectively as shown in Table 5.2.1. This is because the spring season is a rainy season with high temperatures and therefore, when the water temperature increase. The other factor which resulted in high TDS is rain because it adds more minerals and therefore affects the TDS measurements. Nevertheless, the results obtained for TDS measurements for the effluents in the oil refinery depot are within the permissible limits of 0 to 450 mg/L (DWAF, 1996d). High values of TDS concentrations may cause osmotic stress and affect the osmoregulatory capability of the species that inhabit the aquatic environments and hence elevated levels of TDS can be regarded to be toxic (McCulloch et al., 1993; Igbinosa and Okoh, 2009) and can also result in the dehydration of aquatic animals (Bhateria and Jain, 2016).

5.2.2 **Electrical conductivity (EC)**

Electrical conductivity (EC) is the measure of a material's ability to allow the transport of an electric charge and is greatly dependent on the availability of ionic species such that the higher the concentration of ions in the sample, the higher the conductivity. The conductivity measurements of the sample were performed in the field from the pans filled with clear water (control) and OPW and generally they varied significantly ($P < 0.05$). The results presented in Table 5.2.1 show that, the electrical conductivity values for the samples ranged from 515.00 – 569.05 µS/cm during autumn season, 512.13 – 568.00 µS/cm in winter, 518.00 – 592.20 µS/cm in spring season and 538 – 551.00 µS/cm during summer seasons. The higher EC values were observed in spring with the maximum value of 592.20 µS/cm. The same trend was observed with high TDS values obtained in spring. This observation is true because TDS and EC are indirectly related, and a higher conductivity value indicates that there are more organic and inorganic substances dissolved in the water. As revealed by Table 5.2.1, the EC values ranged from 512.13 – 592.20 µS/cm throughout the year and it is not within permissible discharge limit according to the South African guidelines (250 µS/cm) for conductivity of the effluent that could be discharged into the receiving waterbodies (Government Gazette, 1984). However, the value was found to be within the guidelines set by (Department of Water Affairs, 2013) specification of 700 – 1500 µS/cm for discharging into water resources through pipe, canals or sewers.

Discharging the effluent with high concentration of EC into the receiving water bodies may result in water imbalance for aquatic species and could greatly decrease dissolved oxygen concentration (Fatoki, Gogwana and Ogunfowokan, 2003) (Aniyikaiye *et al.*, 2019).

Table 5.2.2 presents the annual trend in terms of physico-chemical parameters measured at an oil depot for the influent and effluent portions of the wastewater. The samples were taken from the influent compartments designated as S1= raw water, S2 = physical treatment process section via skimming and S3 post treatment section. The samples were also taken from the effluent (discharge point) at three different sampling points 1 m apart and were designated as S4, S5 and S6. Table 5.2.2 is providing a general representation of the chemistry of the wastewater and hence a measure of the physico-chemical parameters which provide a reasonable clue on the compliance of the plant.

Table 5.2.2: Physical and chemical characteristics of wastewater of the oil depot

Influent					Effluent		
		S1	S2	S3	S4	S5	S6
BOD (mg/L)	Autumn	8.50 - 23.50 (10.22 ± 2.41)	6.00 - 16.00 (7.26 ± 1.82)	5.00 - 8.00 (6.51 ± 1.27)	2.50 - 2.80 (3.21 ± 0.38)	2.10 - 2.70 (2.71 ± 0.28)	2.16-2.50 (2.53 ± 0.25)
	Winter	7.41 - 23.12 (9.87 ± 1.71)	7.11 -18.11 (9.28 ± 1.62)	6.11-9.11 (5.28±1.21)	2.57-3.91 (3.95 ± 0.47)	2.05 - 3.89 (3.21 ± 0.41)	2.01 - 3.71 (2.89 ± 0.49)
	Spring	5.52 - 19.86 (9.12 ± 0.68)	4.51 - 18.86 (8.72 ± 0.68)	2.32 - 3.51 (3.61 ± 0.31)	2.42 - 3.47 (3.57 ± 0.35)	2.09 - 3.52 (3.41 ± 0.41)	2.42 -3.91 (3.21 ± 0.38)
	Summer	6.11 - 20.00 (9.47 ± 0.51)	5.71 - 19.86 (9.2 2± 0.51)	3.32 - 4.35 (3.61 ± 0.39)	3.32 -4.35 (3.61 ± 0.39)	3.10 - 4.27 (3.56 ± 0.35)	3.12 - 4.06 (3.47 ± 0.31)
COD (mg/L)	Autumn	301.00-373.00 (337.61± 29.50)	235.00 - 328.71 (294.26±31.75)	204.17 - 295.15 (261.25±31.01)	233.00 - 332.29 (297.71 ± 10.36)	258.61 - 371.00 (254.02 ± 17.21)	250.00 - 256.33 (254.43 ± 3.67)
	Winter	239.00 - 440.2 (337.35± 33.39)	209.00 - 324.14 (298.60 ±28.12)	179.00 - 291.5 (259±27.49)	142.20 - 399.67 (245.31 ± 14.58)	271.00 - 331.00 (238.90 ± 8.78)	230.33 - 263.44 (243.92 ± 7.04)
	Spring	375.00 - 517.00 (356.76 ±30.15)	341.00 - 432.00 (320.00±27.50)	158.00 - 388.00 (282.38±25.20)	209.11 - 321.00 (257±6.81)	236.00 - 305.00 (251±6.21)	218.33 - 295.43 (249.39 ± 5.27)

	Summer	301.00 - 357.00 (331.58 ± 17.80)	217.00 - 243.00 (299.20 ± 17.57)	235.00 - 293.00 (266.12 ± 18.66)	251.00 – 265.00 (257± 8.11)	247.00 – 259.00 (255 ± 8.65)	240.00 - 251.13 (252.46 ± 8.67
TOC (mg/L)	Autumn	249.00 - 311.00 (265.76±14.22)	195.00 - 255.00 (208.50±13.44)	180.00 - 240. 00 (193.48±13.43)	101.18 - 112.52 (110.00 ± 2.53)	102.17 - 110.27(109.67 ± 2.50)	101.67 -107.67 (107.99 ± 2.48)
	Winter	251.00 - 302.00 (241±12.11)	194.00 – 245.00 (233±11.87)	180.00 - 230.00 (147±9.24)	108.22 - 158.21 (133.21 ± 4.27)	106.51 -155.12 (130.12 ± 4.16)	104.67 -143.67 (128.27 ± 5.48)
	Spring	256.00 - 276.00 (268.14±10.26)	200.00 - 265.00 (247.00±9.21)	174.00 - 240.00 (141.01±8.21)	110.00 - 164.19 (133 ± 5.10)	107.25 - 156.21(132.10±4.57)	111.67 - 150.67 (130.16 ± 7.73)
	Summer	273.00 - 301.00 (281.10±13.57)	217.00 - 243.00 (231.05±8.18)	202.00 - 228.00 (210.21± 8.70)	127.21 - 141.00(129.28±5.97)	115.01 - 133.71(127.22±5.50)	113.67 - 129.70 (124.08 ± 5.70
TSS	Autumn	160.22 - 198.98 (178.4 ± 12.62)	117.23 - 156.13 (137.40 ±12.17)	57.69 - 95.91 (75.55 ± 12.21)	45.93 - 84.51 (63.57 ± 12.59)	32.41 - 83.13 (61.062 ± 11.41)	44.17 -53.26 (51.20 ± 3.42)
	Winter	158.26 - 193.03 (174.01 ± 8.13)	117 - 152.15 (133.30 ± 8.15)	50.00 -90.27 (71.58 ± 8.24)	42.17 - 57.15(49.89 ± 4.22)	43.21 -51.21 (47.22 ± 4.35)	38.73 -54.49 (51.33 ± 2.19)

(mg/L)							
	Spring	160.87 -200.23 (174.80 ± 9.80)	122.88 - 139.89 (133.90 ± 9.79)	58.11 - 97.47 (72.05 ± 9.79)	46.22 - 60.15 (51.94 ± 2.59)	49.14 - 61.23 (52.29 ± 3.12)	47.38 - 58.24 (53.17± 3.44)
	Summer	159.97 - 186.88 (170.59 ± 9.44)	119.82 - 146.00 (130.70 ±8.66)	59.65 - 84.12 (58.23 ± 7.71)	49.51 - 65.25 (54.27 ± 6.13)	47.19 - 61.28 (55.18 ± 5.22)	48.95 - 55.47 (53.29 ± 5.01)
TPH (mg/L)	Autumn	9.22 - 15.63 (11.41±1.68)	9.22 - 13.17 (11.29± 1.52)	9.16 - 11.71 (10.66 ± 1.22)	9.02 -9.81 (9.89± 1.57)	9.17 - 9.62 (9.53± 0.281)	9.00 - 9.22 (9.20± 0.38)
	Winter	9.16 - 12.71 (10.24± 1.24)	9.17 -11.67 (10.01± 1.13)	9.11 - 11.51 (9.92 ± 1.10)	9.01-10.26 (9.22 ±0.52)	9.21-10.11 (9.17±0.24)	9.14-10.02(9.14± 0.21) 0.46)
	Spring	9.23- 14.04 (12.28± 4.31)	9.31 - 13.95 (11.56± 4.76)	9.56 - 11.29 (10.92±5.6)	9.47 - 10.81 (10.19± 4.01)	9.32-10.33(10.14± 2.9)	9.16 -10.21(10.05± 2.4)
	Summer	9.37 - 11.69 (10.14±063)	9.32 - 11.26(9.84± 0.52)	9.01 - 10.92 (9.34± 0.48)	8.56 - 10.47(9.14± 0.47)	8.39 - 10.30 (9.05± 0.51)	8.23 - 10.14 (9.01 ± 0.46

* S (influent): 1= raw water, 2= treatment section via skimming, 3= post treated water

* S (Effluent) Discharge point: 4= (1 m apart), 5 = (1 m apart) 6=(1 m apart)

Table 5.2.3 shows the annual trend in terms of physico-chemical parameters measured in the oil depot for in the influent and effluent portions of the plant. This Table can provide a general representation of the chemistry of the wastewater and hence a measure of the physico-chemical parameters will provide a reasonable clue on the compliance of the plant.

Table 5.2.3: Annual variations in the physico-chemical parameters of the oil depot effluent.

Parameter	S1	S2	S3	Average	S4	S4	S5	Average	Allowed discharge limit	Comment
BOD (mg/L)	24.04 ± 1.15	18.81 ± 1.16	10.56± 1.22	17.80 ± 1.16	3.03 ± 1.27	3.02 ± 1.31	3.00±1.24	3.01 ± 0.48	-	-
COD (mg/L)	384.07±48.02	276.02 ± 45.44	269.03±24.03	276.38± 45.12	249.88 ± 18.96	247.63±12.32	244.57± 14.74	249.74± 15.97	30	Above the limit
TOC (mg/L)	165.56± 21.95	163.45 ± 18.98	159.35±21.961	162.79± 32.9	123.21 ± 12.61	125.23±11.71	127.27± 12.49	125.25± 11.39	-	-
TSS (mg/L)	175.61±30.51	135.78±29.48	72.15±19.50	127.80±33.57	50.36±	48.54±	±46.95	49.81 ± 4.11	25	Above the limit
TPH (mg/L)	12.85± 5.51	11.32± 3.25	11.07± 4.76	11.75± 4.16	10.15± 3.79	10.39± 5.20	10.00± 4.10	10.02 ± 0.79	-	-

5.2.3 **Measurements of Biochemical oxygen demand (BOD)**

BOD analysis for the collected wastewater samples was determined using a modified Winkler's method using Merck BOD cell test kit. It was essential to monitor the BOD, a parameter which provides a measure of water/wastewater pollution index used to assess the quality of the effluent. This parameter provides a measure of the organic content of the effluent and thus the magnitude of oxygen consumption. Higher contents of organic matter in waters tend to prevent the smooth survival of the aquatic life (Wirnkor, Amonia and Ngozi, 2014). Higher BOD concentrations indicate the greater the extent of oxygen depletion in the water bodies (Aniyikaiye *et al.*, 2019). This means that where there is higher levels of BOD there is little oxygen available for higher forms of aquatic life which can result into the death of aquatic species (Bhateria and Jain, 2016). BOD has the same effects as those of DO to aquatic organisms (depleting dissolved oxygen) which tend to cause stress, suffocation and eventually death of the aquatic species (Bhateria and Jain, 2016) . For this reason, it is always important to assess the BOD level of wastewater prior to the discharge into the receiving water bodies or municipal wastewater channels. The results of this study are presented in Table 5.2.2. A total of seven different physiochemical parameters including BOD were investigated. The analysis was based on the samples taken from the oil depot (petroleum industry). The BOD blanks were analysed along with the samples to check the quality of the dilution water. The dissolved oxygen uptake of the dilution water was 0.05 ± 0.02 mg/L. Normally, more than 0.20 mg/L indicates possible contamination or calibration error.

The BOD values for OPW generally varied significantly ($P < 0.05$). The influent results (Table 5.2.2) shows that BOD ranged from 2.10 to 23.50 mg/L during autumn; 2.01 to 23.12 mg/L during winter; 2.09 to 19.86 mg/L during spring and 3.10 to 20.00 mg/L during summer. Particularly, the BOD of the treated final effluent varied between 2.01 and 4.06 mg/L for the entire seasons. (Ehiagbonare and Ogunrinde, 2010) obtained similar results of low BOD results where BOD values ranged between 1.69 - 3.38 mg/L for the fishponds in different locations in Okada and its surroundings, in Edo State, Nigeria. There is no standard guideline set for the control of BOD for wastewater in South Africa, but it is important to measure it because BOD and COD in many times gives indications of the extent of organic pollution in water and wastewater (Edokpayi, Odiyo and Durowoju, 2017).

5.2.4 **Chemical Oxygen Demand (COD)**

The oxidation of organic and inorganic compounds wastewater effluent discharges from industrial channels tends to deplete the dissolved oxygen supply in a receiving water (Jirka and Carter, 1975). Chemical oxygen demand (COD) refers to the ability to consume oxygen in the form of potassium dichromate during the degradation of organic matter and inorganic chemicals such as nitrite and ammonia for a specified time period (Samudro and Mangkoedihardjo, 2014). The COD measurements were prepared with COD blanks (1.204 ± 0.02 mg/L) and this was to ensure that there were no organic materials added accidentally to the sample being measured. The blank sample was constituted with water (chromasolv) from Merck-Millipore instead of the sample. The results as presented in Table 5.2.2 shows that during autumn the COD values for treated wastewater (effluent) ranged from 256.00 to 271.00 mg/L; whereas during winter the values were from 230.33 to 263.45 mg/L and during spring and in summer COD valued stood at 219 to 283.67 mg/L and 238.33 to 267 mg/L respectively. Generally, the COD value for OPW values ranged from 142.20 to 399.67 mg/L throughout the year. The COD values obtained in all seasons are above the recommended discharge limit according to South African standards for the discharge of the effluents which is0-10 mg/L (DWAF and WRC, 1995), 30 and 75 mg/L for special and general standard respectively (Government Gazette, 1984) and 75 mg/L (Department of Water Affairs, 2013). The wastewater analyzed for COD from influent compartment at three sampling points for all seasons labeled as S1, S2, and S3 were found to have annual average COD values of 384.07 ± 48.08, 276.02 ± 45.44 and 269.03 ±24.03 mg/L respectively. The average COD as obtained for final effluent treatment was 249.88 ± 18.96, 247.63 ± 12.32 and 244.57 ± 14.74 mg/L for S3, S4 and S6 respectively (Table 5.2.3). However, despite these reduction efficiencies, the resulting COD values greatly exceeded the limits for effluent discharge. Depending upon concentration and source of contamination, an alternative treatment technique that may provide the required efficiency is required to reduce the toxic level of pollutants (Bennett and Peters, 1988; Sonune and Ghate, 2004; Hanafy and Nabih, 2007; Farajnezhad and Gharbani, 2012; Li *et al.*, 2014; Padaki *et al.*, 2015). Elevated levels of COD in samples may be due to the presence of oxidizable organic matter in large amount, which reduce the DO levels. Therefore, it is not safe to discharge effluents with high level of COD to the receiving bodies or municipal channels.

5.2.5 **Total organic carbon (TOC)**

Total organic carbon (TOC) refers to the amount of carbon found in the matrix (sample) and is often used as a non-specific indicator of water quality. Statistical analysis using the analysis of variance (ANOVA) for samples from an oil depot revealed that in most cases, there were significant differences ($P<0.05$) in the TOC values of samples collected from different sampling points (S1-S6). Generally, the TOC measurements obtained from the influent compartment ranged from 180.00 to 311.00 mg/L and 101.18 to 169.14 mg/L for the treated wastewater (Table 5.2.2) for the entire study period o. There is no set standard for TOC level for effluent discharge into the receiving water bodies in South Africa but it is important to measure it because it gives an indication of the level of organic contamination and water purity and as well for avoiding the growth of pathogenic microorganisms. Apart from this reasoning, the reduction of organic carbon before the disinfection process for drinking water purification can decrease the possible public exposure to dangerous byproducts because organic carbon reacts with chemicals used for disinfection such as chlorine. This can result into the formation of disinfection byproducts which are known to be carcinogenic.

5.2.6 **Total suspended solids (TSS)**

The measure of the total suspended solids (TSS) is normally used to reveal the extent of pollution in wastewater. TSS refers to particles that are not dissolved in a sample but are suspended and can be trapped by a filter by means of a filtration apparatus. In this work, the results for TSS analysis showed that the TSS concentrations of the raw and treated final effluent varied significantly ($P < 0.05$). The average TSS values for the raw wastewater were found to be 160.22 - 198.98 (178.4 ± 12.62), 117.23 - 156.13 (137.40 ±12.17) and 57.69 - 95.91 (75.55 ± 12.21) mg/L for S1, S2 and S3 sampling points respectively. For the effluents, TSS values were 45.93 - 84.51 (63.57 ± 12.59), 32.41 - 83.13 (61.062 ± 11.41) and 44.17 -53.26 (51.20 ± 3.42) mg/L for treated effluent S3, S4, and S5 sampling points respectively for autumn season (Table 5.2.2). In winter season the observed TSS values were, 158.26 - 193.03 (174.01 ± 8.13), 117 - 152.15 (133.30 ± 8.15) and 50 -90.27 (71.58 ± 8.24) for S1 , S2, and S3 respectively whereas for the final treated effluent; 42.17 - 57.15(49.89 ± 4.22), 43.21 -51.21 (47.22 ± 4.35), and 38.73

-54.49 (51.33 ± 2.19) respectively. During the spring season the TSS level were 160.87 -200.23 (174.80 ± 9.80), 122.88 -139.89, (133.90 ± 9.79) and 58.11 - 97.47 (72.05 ± 9.79) for S1, S2, and S3 respectively and from the treated 46.22 - 60.15 (51.94 ± 2.59), 49.14 - 61.23 (52.29 ± 3.12), 47.38 - 58.24 (53.17± 3.44) for S3, S4, and S6 respectively. TSS concentrations for S1, S2, and S3 were 159.97 - 186.88 (170.59 ± 9.44), 119.82 - 146.00 (130.70 ±8.66) and 59.65 - 84.12 (58.23 ± 7.71) mg/L respectively and from the treated effluent the TSS values were (55.18 ± 3.13), (55.18 ± 3.22), and 48.95 - 55.47 (53.29 ± 3.01) respectively during summer season as shown in Table 5.2.2. Based on the South African guidelines, the TSS of the effluent appears to pose threat to the receiving water bodies because is not within the discharge limit of 25 mg/L (Department of Water Affairs., 2013) . This showed that the physical treatment of skimming was not efficient enough in reducing the level of TSS concentrations. Exposure to water with high levels of TDS and TSS put people at risk of cancer (Kaur *et al.*, 2010).

5.2.7 **Total petroleum hydrocarbons (TPH)**

Total petroleum hydrocarbons (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil which is used to make petroleum products, The average TPH results for influent and effluent samples analyzed were 12.85 ± 5.51, 11.32 ± 3.25, 11.07 ± 4.76 10.15 ± 3.79, 10.39 ± 5.20, and 10.00 ± 4.10 mg/L for S1, S2, S3, S4, S5, and S6 respectively (Table 5.2.3). From the TPH results obtained it was observed that the profile throughout the year covering all seasons varied significantly ($P < 0.05$) To our best of knowledge, there is no set standard for TPH level for effluent discharge into the receiving water bodies in South Africa. The results from this work has revealed that the total mean concentration of TPH for the samples analyzed was (10.02 ± 0.79 mg/L) (Table 5.2.3) and in all the effluent points were higher than the EU acceptable standard limit for 0.30mg/L for hydrocarbons in estuary and harbor basin water (Adeniji, Okoh and Okoh, 2017). Even though South Africa remains one the largest economies in the continent, not many studies have documented the concentrations of TPH in its environmental resources (Adeniji, Okoh and Okoh, 2017). From a few studies conducted in South Africa, that the higher TPH concentrations were reported at E1(Buffalo River inflow) and E3 (second creek) in a study conducted by Adeniji, Okoh and Okoh, 2017 in the Eastern Cape Province of South Africa. In their study, they concluded that it may be due to the leachate from a dumpsite close by, industrial effluent discharge, and

urban/agricultural runoffs. Hence this study saw the necessity to include TPH as one of the parameters to be investigated. Based on the results obtained, it is suggested that the effluents should be subjected to secondary treatment since the primary treatment could not reduce the contamination level and make it in allowed limit for discharge into water bodies. Secondary treatment includes coagulation, flocculation, and further biological treatment to reduce toxicity of petroleum wastewater (Xu and Zhu, 2004 ; Viggi *et al.*, 2015; Changmai *et al.*, 2017).

5.3 **Prediction of compliance of oil produced water using the evaporation rate patterns.**

Evaporation is a very important component of the hydrological cycle. Estimates of evaporation rates from open water bodies are required in water resource management for multiplicity purposes. Some examples of the application of evaporation rates include the abstraction licensing, design of reservoirs catchment water balance studies and management of wetlands (J W Finch and Hall, 2001). The demand for such estimates is of utmost importance in this work as it will make it possible to use the evaporation patterns to predict the level of compliance of wastewater that is discharged as oil produced water at an oil depot. An important step to the understanding of evaporation is to understand the mechanisms, and therefore all the major factors that control open water evaporation were investigated in this work.

5.3.1 **Estimation of oil produced evaporation**

A widely used class A pan (U.S. Department of Commerce 1970), was employed in this study to measure the rates of evaporation. Two class A pans were installed in the field and one of pan was filled, with clearwater (control) and the other with oil produced water (OPW). The former was installed to measure the clear water evaporation (CWE) and the latter oil produced evaporation (OPWE). The environmental parameters that were investigated included EC, TDS and water temperature and they were measured from both the clearwater and OPW pans.

It should be noted that, very rarely pan evaporation measurement are used directly as estimates of evaporation from water body because of the scale discrepancy affecting the ambient sensible heat fluxes (J. W. Finch and Hall, 2001; Izady *et al.*, 2016). The use of data obtained from the pans situated away from the water body could result in considerable errors (Winter, 1981). Due to this, the correction factor need to be applied by multiplying the observed yearly total pan

evaporation by an empirical "pan factor" which, is approximately 0.7 as in the case of the American class A pan as suggested by (Webb, 1966).

5.3.2 **Clear water evaporation (CWE) v/s oil produced water evaporation (OPWE)**

The main aim for this work was to use the evaporation patterns to predict compliance of effluents discharged from OPW. CWE was used as reference for control purposes. The results depicted in Figure 5.1 show that the mean evaporation rate for clear water ($\overline{x}$ = 3.98 mm/day) and this was found to be significantly more than the evaporation from effluent from the discharge point compartment ($\overline{x}$ = 1.94 mm/day). The clear water evaporation rate was found to be 2-fold higher than the evaporation rates for the OPW.

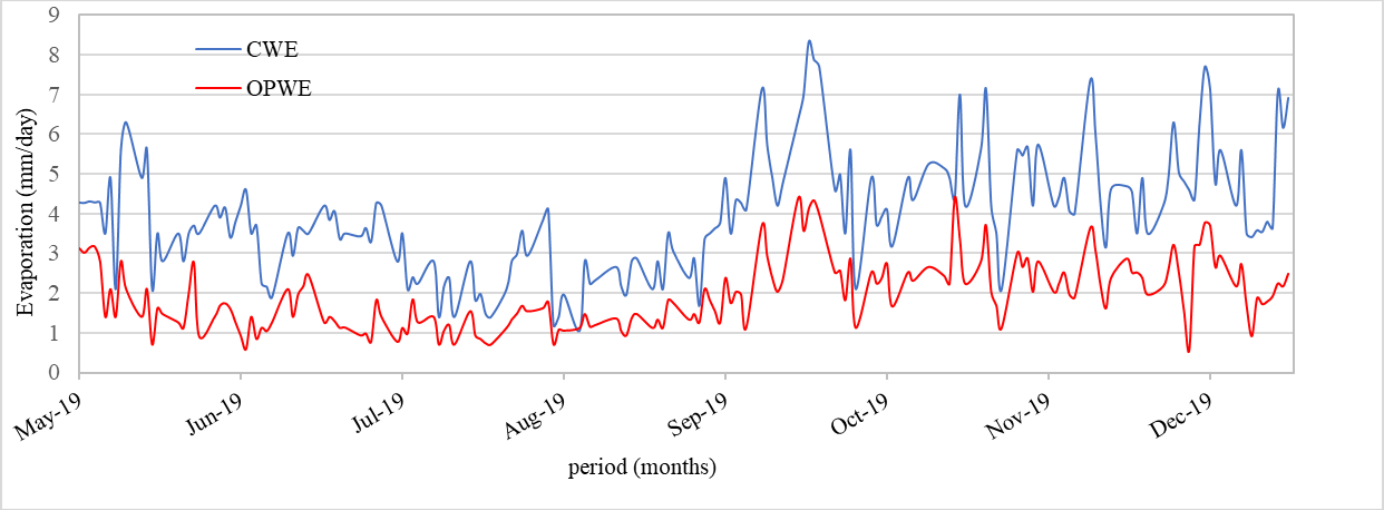

Fig. 5.1 Variation trends of CWE and OPWE for the period from May to December 2019

The evaporation of a liquid is due to the movement of molecules from the surface into the vapor phase above it. There are many factors which contribute to the rate of the evaporation of the liquid. Figure 5.1 shows the relation of proportionality between CWE and OPWE. However, the CW shows to evaporate more than OPW. This observation agrees with literature because theoretically, oil do not mix with water and oil is less dense than water (including the crude oils). Therefore, this will cause the oil to float on top of the water and form a thin layer depending on the type of the oil thus hindering the evaporation of the liquid water underneath. Light oils changes drastically from fluid to viscous and Heavy oils becomes solid-like (Fingas, 2015). This resulted in the evaporation of OPWE to be lower than that for CWE.

5.3.3 **Effect of the climatic parameters on the rate of evaporation**

Evaporative demand is measured directly by Epan (evaporation from the pan) (Roderick *et al*., 2007) and is mostly strongly influenced by climatic parameters which include solar irradiance, temperature, humidity and wind speed (Roderick and Farquhar, 2002; Roderick *et al*., 2007). The climatic/meteorological factors that have notable effects on the evaporation process are air temperature, water temperature, solar radiation, and wind speed.

5.3.4 **Air temperature (T_a)**

Statistical analysis of the results for air temperature measurements (Figure 5.2) using ANOVA revealed that in most cases, there were significant differences ($P<0.05$) in air temperature throughout the study with the mean air temperature being ($\bar{x}$ = 20.20° C) (Table: 5.2.4).

Table 5.2.4: Annual variation of the evaporation and climatic parameters.

parameters	Mean	SD
CWE (mm/da)	3.98	1.51
OPWE (mm/day)	1.94	0.86
Ta (°C)	20. 20	5.93
Tcwe (°C)	25.37	6.66
Topw	28.08	6.71
W (m/s)	3.23	0.92
R (W/m^2)	6.20	2.04

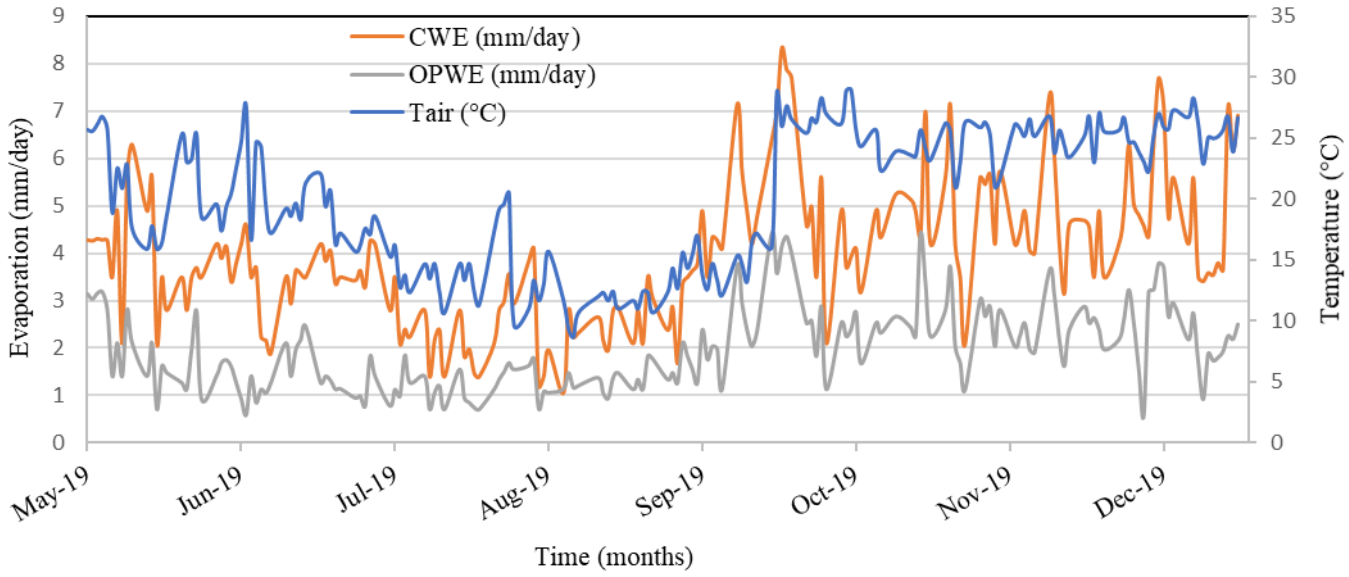

Figure 5.2: Variation trends of monthly evaporation rates vs air temperature for the period of May to December 2019

Variation trends of monthly evaporation rates vs air temperature for the period from May toDecember2019.

Figure 5.2 shows that there is a directly proportional relationship between the evaporation rates and the air temperature. Figure 5.2 depicts the monthly effluent evaporations for the period covering May – December 2019. The magnitude of evaporation was at its maximum in spring (September to November) and summer (December) and low in June – August 2019 because South Africa has typical weather of the Southern Hemisphere, with the coldest days in June–August. The rising trends of air temperature from September to December resulted into increased rates of evaporation. This is because higher temperature results into movement of more molecules from the bottom to the water surface with high speed thus causing increasing escape as vapor and furthermore high temperature causes intensive molecule diffusion into surrounding space (Vuglinsky, 2009).

5.3.5 **Solar radiation**

Figure 5.3 shows that the evaporation rates varied significantly over the open-water season throughout the year of the study ($P<0.05$), and the pattern of variation was not consistent from month to month.

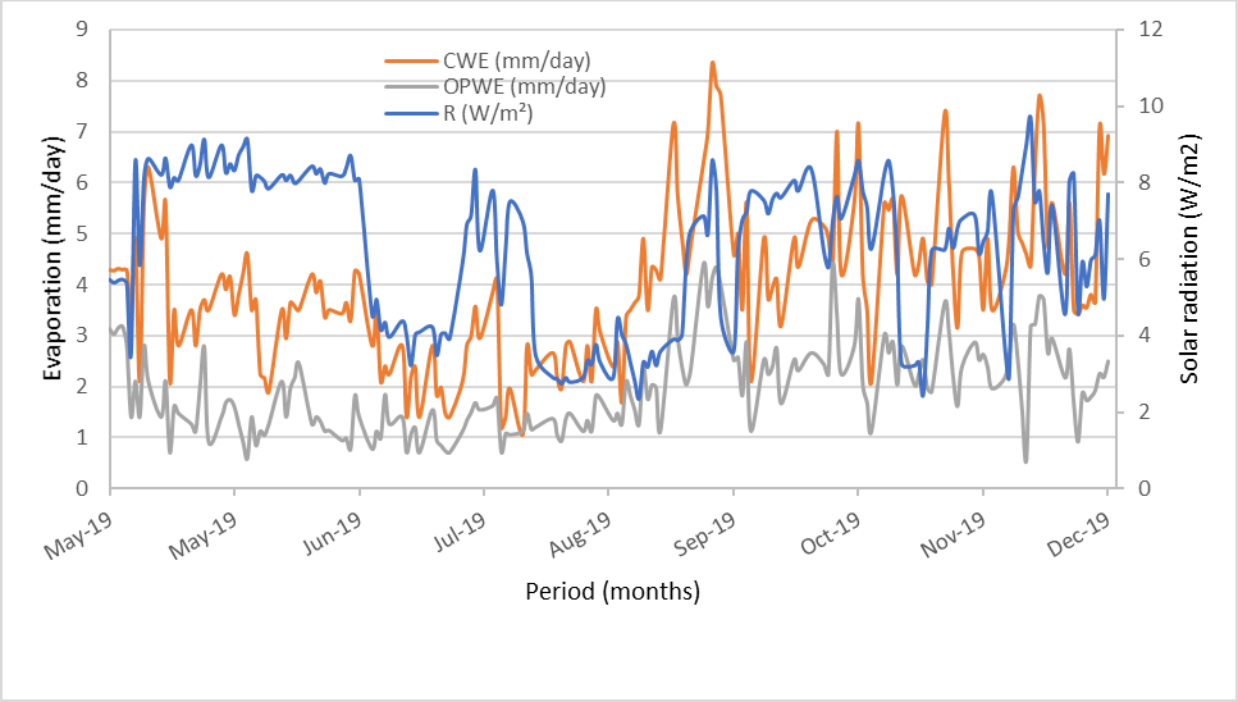

Figure 5.3: Variation trends of monthly evaporations and solar radiation for the period of May to December 2019.

There's a harmonious relationship between solar radiation and the evaporation rates, that is, the rate of evaporation of OPW and CW increased with the increase in the solar radiation intensity (Figure 5.3). This trend and observation can be explained from the fact that, solar radiation is a source of energy to molecules and thus the higher the solar radiation bombarding the water surface tends to increase the kinetic energy in order to overcome forces of cohesion thus resulting in the increased evaporation rates The results depicted in Figure 5.3 show that the evaporation rates were at its maximum when the solar radiation was high though not in the same order of magnitude. Based on the total mean of CWE and OPWE of 3.98 and 1.94 mm/day respectively (Table 5.2.4), the CWE was found to be at 2-fold higher than that of OPWE. This observation is fully logical, because solar radiation can penetrate at greater depth enhancing the evaporation rates of clear water whereas, the layer on top of the OPW hindering the solar radiation penetration which results in lower evaporation rates compared to that of clear water. Lower evaporation rates were observed when the solar radiation was at its minimum implying that during the evaporation process, not enough energy reached water, therefore the water cooled and resulted in lower evaporation rates.

5.3.6 **Wind speed**

Figure 5.4 depicts the results obtained that indicate the relationship between the wind speed (W) and the rate of evaporation.

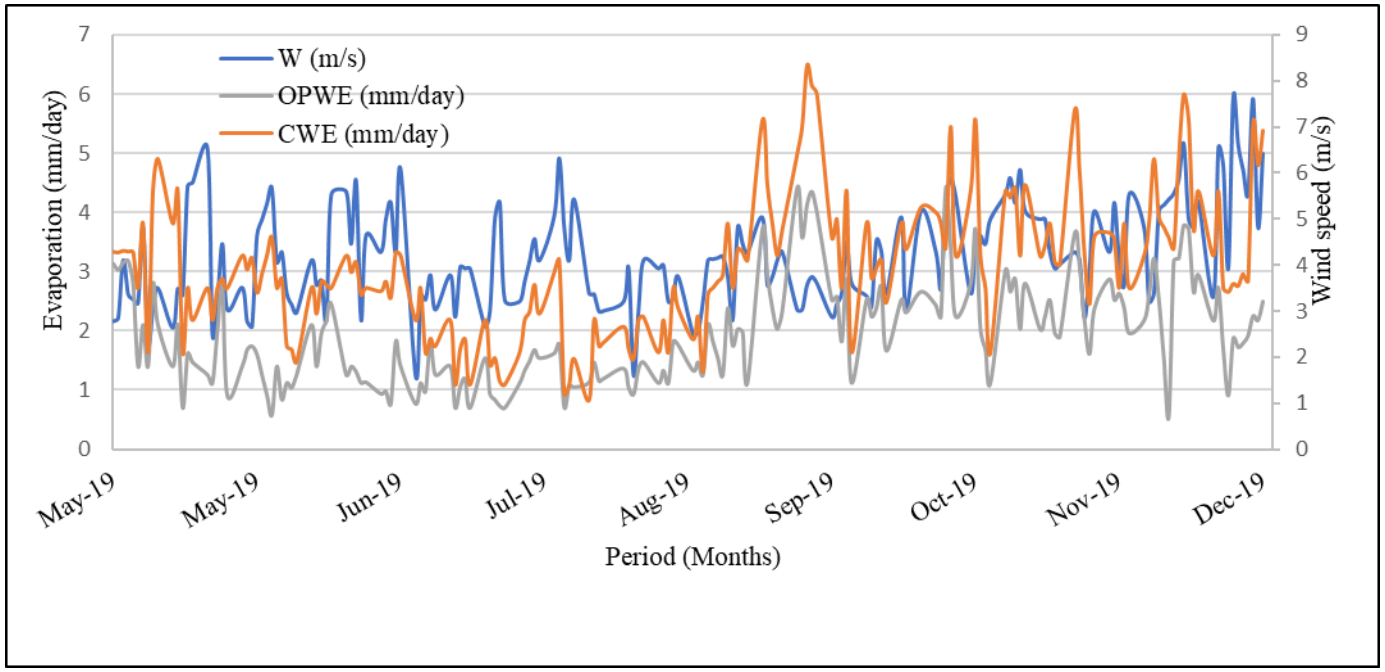

Figure 5.4: Variation trends of monthly evaporations and wind speed for the period of May to December 2019.

The relationship between wish speed seem to be directly proportional to the evaporation rates. Wind speed values were greater in the dry summer months than the winter months (Figure 5.4). This observations was similar to that reported by Hoffman *et al.*, (2011) whereby in their study where they investigated the changes in Epan, wind speed, rainfall, temperature, and vapor-pressure deficit from 1974 to 2005 taken from 20 climate stations in the Cape Floristic Region (CFR), South Africa. They further suggested that the Epan reduction was likely due to the decrease in wind speed. In addition, this study has found that, no statistical significance detected for wind speed throughout the period ($p<0.05$).

5.3.7 **Water temperature (Tw)**

Figure 5.5 indicates how the water temperature affects the rates of evaporation.

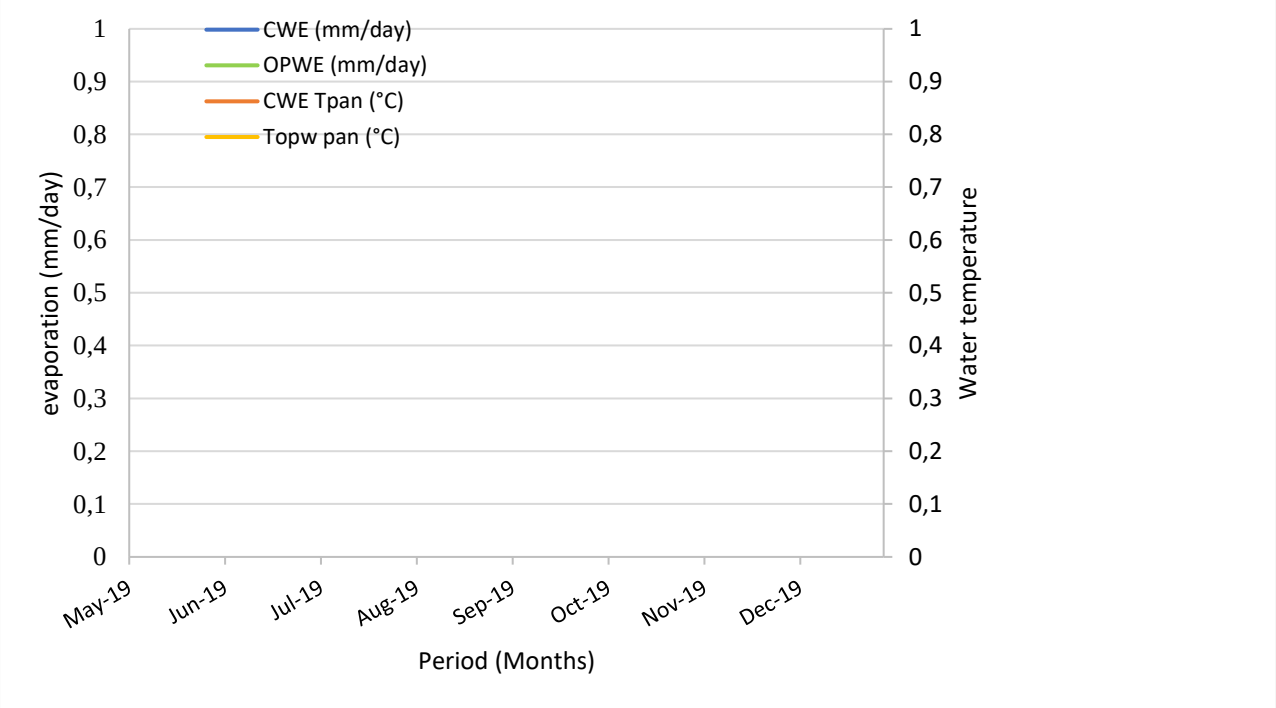

Figure 5.5: Variation trends of monthly evaporations and water temperature for the period of May to December 2019.

The trend observed suggest that the rate of evaporation tend to increase with an increase in water temperature (Figure 5.5). This is because the water molecules move rapidly when heated thus making the water molecules to escape faster. Higher temperatures lead to increase in vaporization as more molecules get kinetic energy to convert into vapor and then escape. The evaporation rates of clear water were less during winter (June – August) due to the water becoming cooler however the same trend was not observed for oil produced water because waste water has the ability to store energy thus the evaporation rates of oil produced water were high during winter (June- July).

5.4 **Effect of the climatic parameters on the rate of evaporation**

Environmental factors effecting evaporation process including EC, TDS, TSS, TOC, COD, BOD and TPH are discussed below:

5.4.1 **Total dissolved solids (TDS)**

The influence of TDS was investigated, and the results are depicted in Figure 5.6

Figure 5.6: Variation trends of monthly evaporations and total dissolved solids for the period of May to December 2019.

Figure 5. 6 shows the variations of TDS relative to the evaporation rate. This study found that, the TDS measure was directly proportional to the rate of evaporation. This observation can be explained from the fact that the more the ions are present in water the higher the absorption of solar radiation which is a source of energy to molecules giving them enough energy escape the surface. The elevated level of TDS was observed during summer thus leading to high level of OPWE.

Statistical analysis using ANOVA revealed that there were significant differences ($P<0.05$) in TDS values throughout the study.

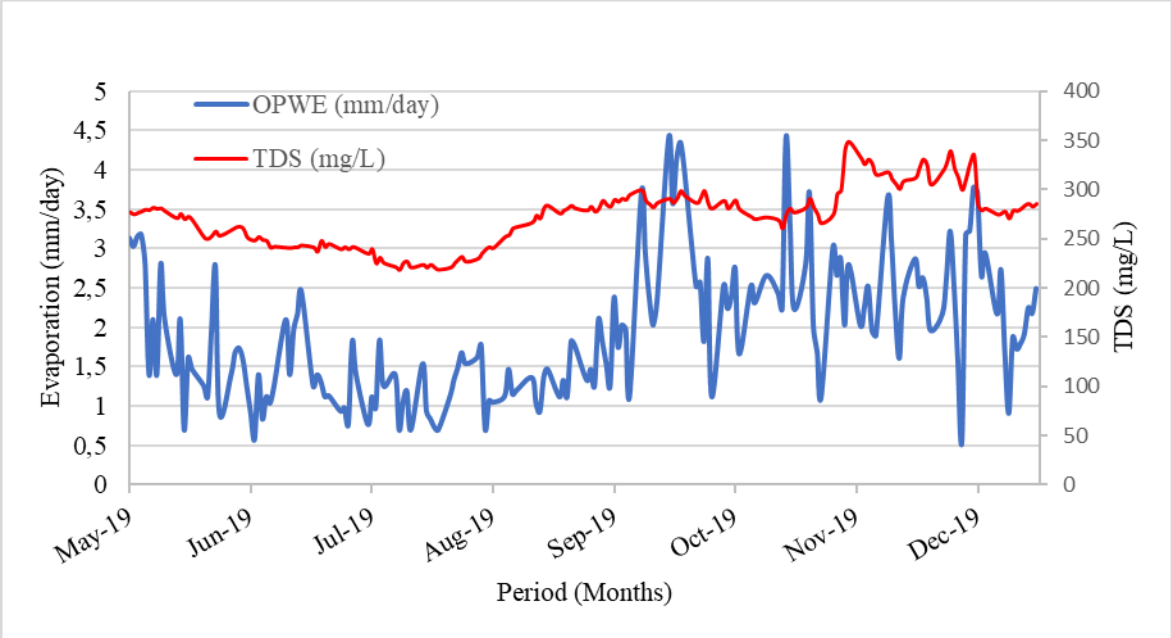

Figure 5.6: Variation trends of monthly evaporations and total dissolved solids for the period of May to December 2019.

5.4.2 **Electrical conductivity (EC)**

There is a direct correlation between EC and the evaporation rates (Figure 5.7). The mean EC for clear water and the effluent was 331.62 and 546.20 µS/cm respectively. This observation is fully justifiable because pure water is generally a poor conductor of electricity. Conductivity depends on the water temperature. The increase in temperature results in increase in conductivity thus an in increase in the rate of evaporation. By measuring the conductivity, the ions in the water is also indirectly being measured and the higher the ions, the higher the electrical conductivity. Therefore, high level of EC is associated with polluted water since some aquatic species cannot survive in elevated concentration of EC. This corresponded with the fact that the effluent did not comply with the regulatory standard of 250 µS/cm (Government Gazette, 1984) as mentioned above.

In addition, no statistical differences were observed among EC concentrations.

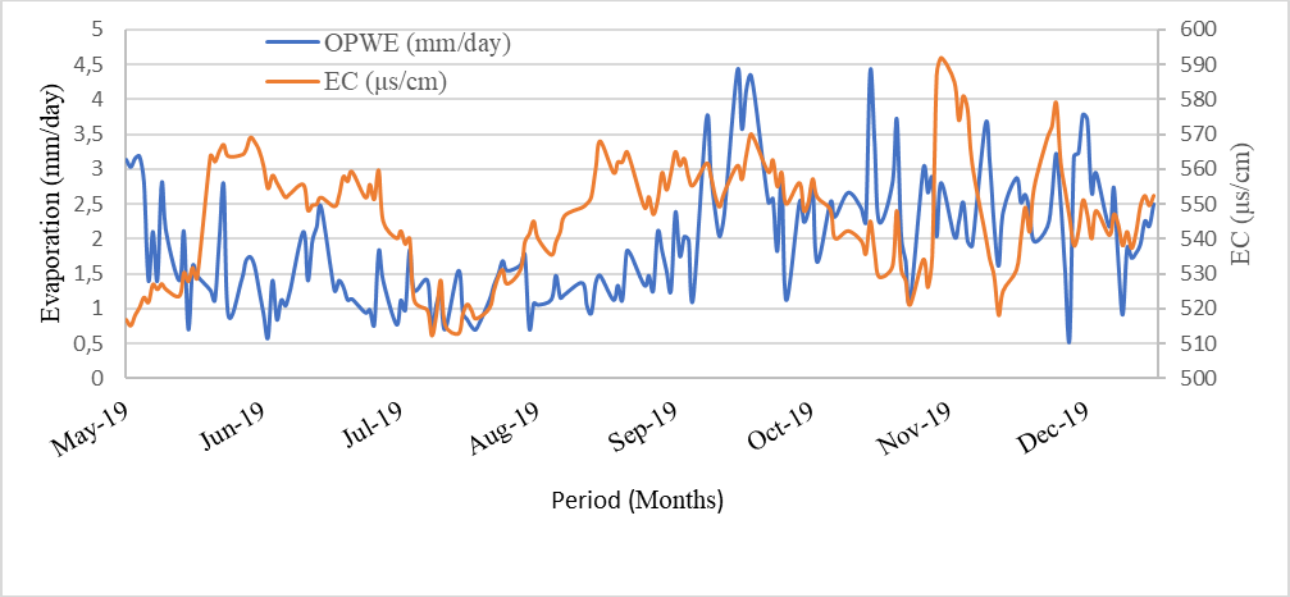

Figure 5.7: Variation trends of monthly evaporations and electrical conductivity for the period of May to December.

5.4.3 **Organic carbons (BOD, COD, and TOC)**

The maximum values of the organic carbons were observed in summertime with the mean of 3.21, 249.39, 130.00 ,160.00 mg/L for S1, S2 and S3 respectively. Figure 5.8 shows an empirical relationship between the evaporation rates and the organic matter parameters. The higher the organic content or carbon , the more oxygen is consumed. A high organic content implies the increase in the growth of microorganisms which contribute to the depletion of oxygen supplies. The trend suggests that the reduction in the evaporation rate results in the reduction of pathogenic microorganisms. This observation is genuine because it is known that aquatic bacterioplankton are sensitive to sunlight radiation, especially in the shortest-wavelength fraction of UV radiation (Herndl, Mi and Frick, 1993) (Sommaruga *et al.*, 1997)(Sommaruga *et al.*, 2005)(Alonso-Sáez *et al.*, 2006). Moreover, Alonso-Sáez *et al.*, (2006) conducted a study to investigate the effects of natural sunlight on heterotrophic marine bacterioplankton and the results suggested that UV radiation can significantly affect the in-situ single-cell activity of bacterioplankton and the naturally dominating phylogenetic bacterial groups have different sensitivity to natural levels of incident solar radiation. Surface solar radiation levels also photochemically degrade bacterial extracellular enzymes. Therefore, increased UV-B radiation due to the destruction of the stratospheric ozone layer might have led to a reduced bacterial activity and the corresponding increased concentration of labile dissolved organic matter in the surface layers of the ocean as bacterial uptake of this is retarded (Herndl, Mi and Frick, 1993).

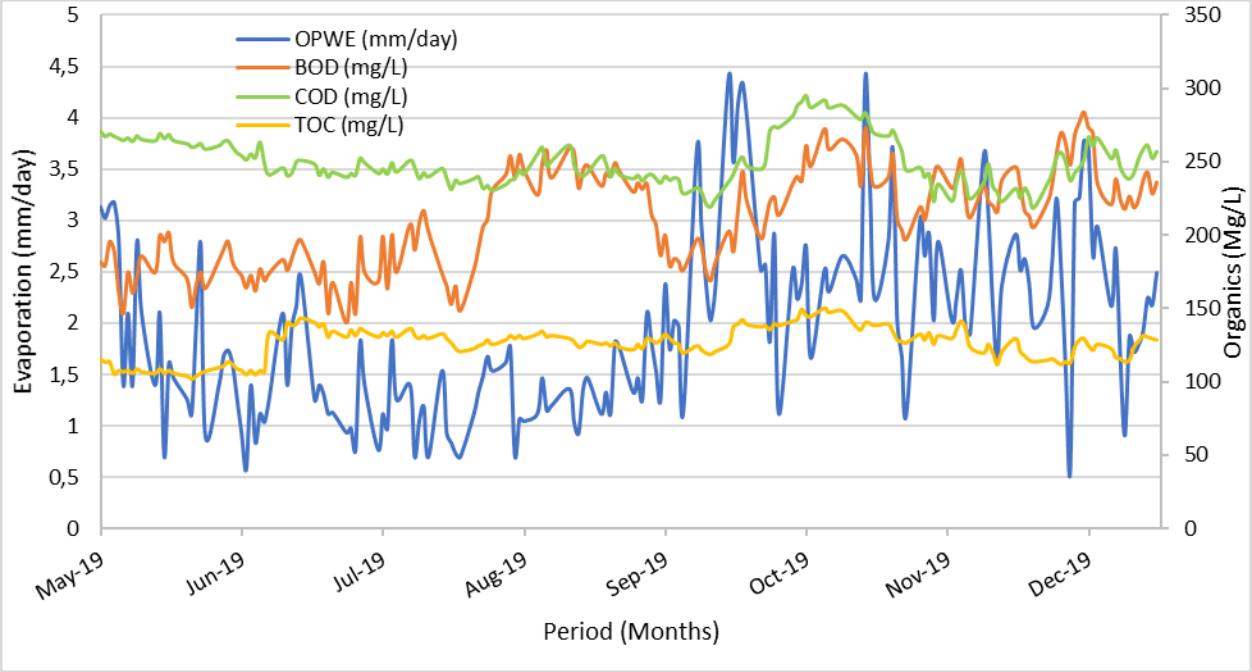

Figure 5.8: Variation trends of monthly evaporations and organic matter parameters for the period of May to December 2019.

5.4.4 **Total suspended solids (TSS)**

As stated earlier, the TSS concentration varied significantly ($p<0.05$). This study has also found that, the rate of the evaporation for both CW and OPW was proportional to the TSS concentrations. The TSS values were high during summer (September to November 2019) season as pointed out above thus leading to more absorption of solar radiation hence the rise in temperature which resulted into the elevated evaporation rates. Therefore, high level of TSS is associated with polluted water since elevated level of TSS may settle out onto a lake or streambed bottom and cover aquatic organisms, eggs, or macro-invertebrate larva (Whitman College, 2015). This coating can prevent enough oxygen transfer a which may lead to the death of buried organisms. Its formation is dependent primarily on the physical processes driven by hydrological phenomena. This corresponded with the fact that the effluent didn't comply with the regulatory standard of 25 mg/L (Department of Water Affairs, 2013) as mentioned above.

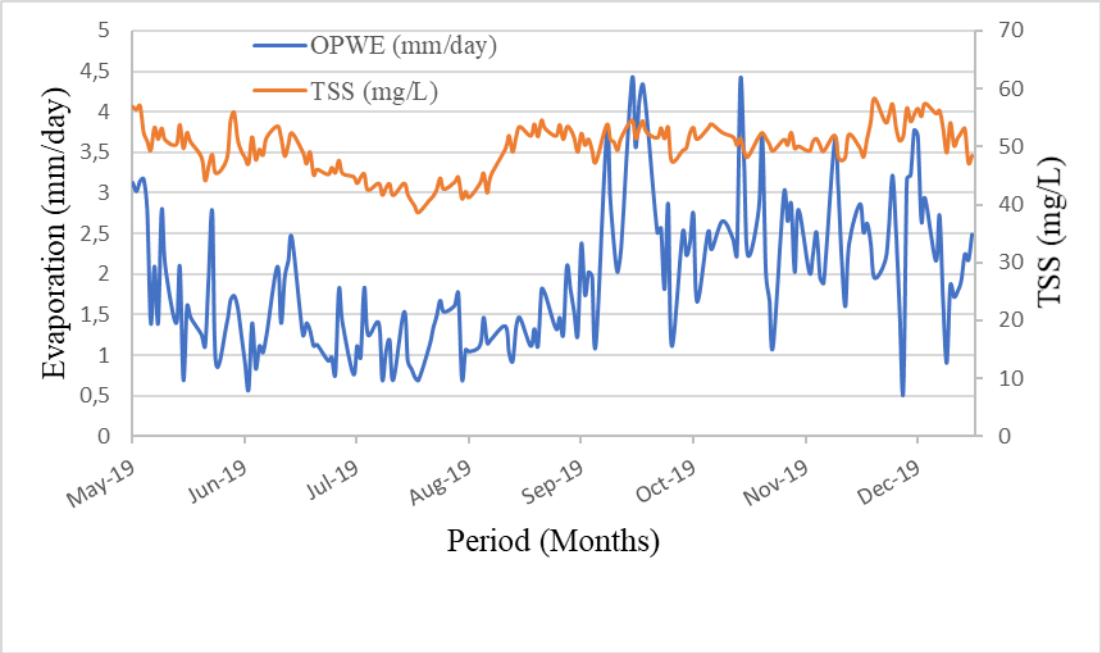

Figure 5.9: Variation trends of monthly evaporations and total suspended solids for the period of May to December 2019.

5.4.5 **Total petroleum hydrocarbons (TPH)**

As pointed before, there was significant variations of TPH concentration ($p < 0.05$) throughout the study. Figure 5.10 shows that, the rate of effluent evaporation and TPH had a direct proportional relationship. The presence of TPH in the wastewater resulted in lower evaporation rates compared to that of clear water. This is because the higher the concentration of TPH, the more oil in the water thus resulting in the lowering of the evaporation rates due to the increased diffusion distance through the liquid. Moreover, certain TPH fractions floats in water and form thin surface films thus hindering the escape of molecules from the surface (Todd, Chessin and Colman, 1999).

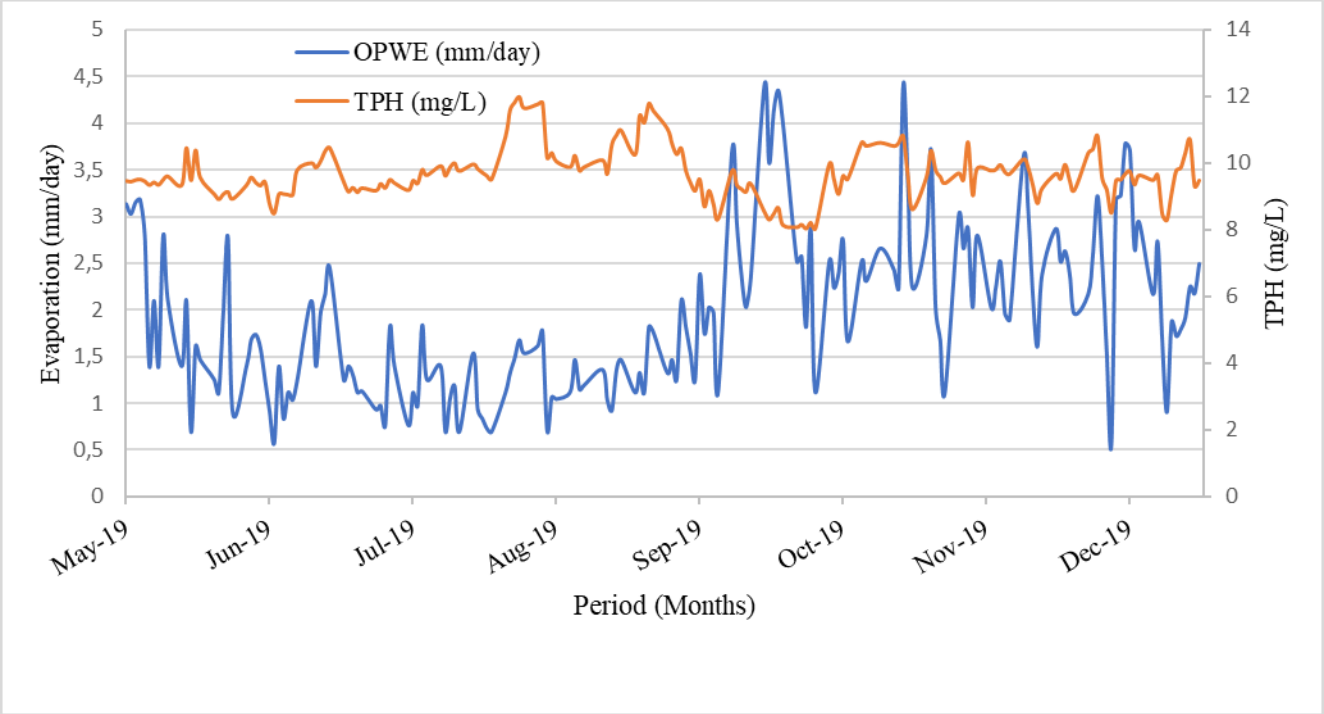

Figure 5.10: Variation trends of monthly evaporations and total suspended solids for the period of May to December 2019.

5.4.6 **Comparison with literature data**

The values for various physicochemical parameters for OPW obtained from this work, was compared with others reported in the literature. Table 5.3 shows this comparison, whereby the values from this work are in some cases very different from some values previously reported. This was expected and can be attributed from the fact that, the chemistry of OPW from different industries will present different characteristics and properties as they will be characteristic to that industry or geographical location.

Table 5.3: Comparison of petroleum effluent data from present study with data from previous studies

Effluent characteristics	Sources					
	Demirci et al., (1998)	Zenga et al., (2007)	Dincer et al., (2008)	Saber et al., (2014)	(Varjani, Kumar and Rene (2019)	This work
pH	6.5-8.5	6.5-6.8	2.5	6.7	6.0-8.5	-
Chemical oxygen demand	800.00	500-1000	21000	450.00	125.00	249.74
Biochemical oxygen demand	350.00	-	8000.00	174.00	15.00	3.01
Total suspended solids	150.00	3000-5000	2580.00	150.00	20.00	49.81
Total dissolved solids	-		37000.00		6200.00	
Total organic carbon	-	-	-	119.00	-	125.25
Oil and Grease	3000.00	400-1000	1140.00	870.00	5	-
Lead	-	-	-	-	0.01	-
Nickel	-	-	-	-	1	-
Zinc	-	-	-	-	5	-
Copper	-	-	-	-	1	-
Mercury	-	-	-	-	0.01	-
Benzene	-	-	-	-	0.1	-
Sulphides	17	15-30	-	-	0.5	-

5.5 **The correlation studies**

The correlations among the physicochemical properties were examined throughout the project. Air temperature didn't show any significant correlation with electrical conductivity of both clear water and oil produced water and TDS of clearwater and TOC. However, a strong correlation was observed between wind speed, solar radiation, Clear water temperature, OPWE, oil produced temperature (Topw), TDS of oil produced water, COD, TSS ($r = 0.33, 0.45, 0.58, 0.33, 0.56, 0.64, 0.35$ 0.48, $P<0.05$ respectively) and air temperature with TPH exhibited a negative correlation (-0.34). Wind speed showed no correlation with environmental parameters except for BOD ($r = 0.26$, $P < 0.05$) and it also showed a positive correlation with the climatic parameters, mainly solar radiation, CWE, clear water temperature, oil produced temperature, clear water TDS (0.30, 030, 0.23, 0.22, 0.22; $p<0.05$). Generally, there was a correlation between climatic parameters and environmental parameters with the rate of both clearwater and oil produced water. It was then necessary to perform the correlation study in order to understand the nature of investigated parameters and their species speciation in the effluent and receiving waterbody as well as to use the evaporation pattern to predict compliance of the targeted wastewater. The results for a correlation study are shown in Table 5.2.

Table 5.2.4: Correlation coefficient r for different parameters from the study period

Parameter	Tair (°C)	W (m/s)	R (W/m²)	CWE (mm/day)	Tcwe(°C)	ECcwe (µs/cm)	TDScwe (mg/L)	OPWE (mm/day)	Topw (°C)	TDSopw (mg/L)	*ECopw (µs/cm)*	*BOD (mg/L)*	*COD (mg/L)*	*TOC (mg/L)*
Tair (°C)	1.00													
W (m/s)	0.33	1.00												
R (W/m²)	0.45	0.30	1.00											
CWE (mm/day)	0.58	0.30	0.28	1.00										
Tcwe (°C)	0.33	0.23	-0.25	0.56	1.00									
ECcwe (µS/cm)	-0.07	0.16	0.02	0.04	0.13	1.00								
TDScwe (mg/L)	0.13	0.22	0.05	0.22	0.23	0.31	1.00							
OPWE (mm/day)	0.56	0.15	0.14	0.82	0.54	-0.06	0.20	1.00						
Topw (°C)	0.64	0.22	0.14	0.63	0.58	0.05	0.22	0.56	1.00					
TDS (mg/L)	0.49	0.18	-0.10	0.57	0.71	0.02	0.31	0.58	0.71	1.00				
EC (µS/cm)	0.12	0.07	-0.04	0.26	0.33	0.19	0.10	0.15	0.52	0.43	1.00			
BOD (mg/L)	0.19	0.26	-0.11	0.28	0.55	0.05	0.13	0.40	0.20	0.50	0.16	1.00		
COD (mg/L)	0.35	-0.05	0.37	0.16	-0.12	-0.30	-0.20	0.21	0.08	-0.06	-0.10	0.18	1.00	
TOC (mg/L)	-0.01	0.05	-0.12	0.09	0.18	0.04	0.00	0.19	-0.04	-0.06	0.09	0.38	0.11	1.00
TSS (mg/L)	0.48	0.11	0.10	0.55	0.53	-0.09	0.07	0.61	0.76	0.67	0.33	0.35	0.26	-0.10
TPH (mg/L)	-0.34	0.00	-0.19	-0.19	-0.05	0.09	0.03	-0.05	-0.30	-0.16	-0.14	0.36	-0.04	0.14

OPWE: oil produced water; CWE: clear water evaporation; Tair: air temperature; R: solar radiation, W: wind speed; Topw: oil produced water temperature; Tcwe: clear water temperature; Topw : oil produced water temperature; ECcwe electrical conductivity of clear,water; ECopw: electrical conductivity of oil produced water ; TDScwe: total dissolved solids of clear water; TDSopw: total dissolved solids of oil produced water; TSS: total suspended solids; BOD: biological oxygen demand; COD: chemical oxygen demand; TOC: total organic carbon; TPH: total petroleum hydrocarbon.

5.6 **Conclusion**

Physico-chemical parameters of the effluents from the oil depot were assessed in this study. Most of the parameters were within the acceptable threshold limits except for COD, TPH and EC that slightly surpassed. This means that wastewater from this oil depot should not be directly discharged into municipal channels, rivers and streams unless it undergoes secondary and tertiary treatment processes. Alternatively, the wastewater may under agreement be channelled to local municipality for further treatment since most depot do not have appropriate facilities for post-treatment process; however, the chemical effluent must also adhere to the rules guidelines and regulations of the municipal where the wastewater will be channelled into. Another challenge, will be the large volume of the wastewater generated being and channelled elsewhere since they contain a lot of by-products. The majority of the oil depots employ physical treatment processes which as it proved by the obtained results are not always effective also do not have necessary equipment to check compliance of the chemical effluent. Therefore, this study sought to use the evaporation patterns to predict the compliance of such wastewater. Based on the results obtained, it is possible to use the evaporation pattern. The evaporation and correlation study supported the hypothesis. As shown by the evaporation patterns that most of the time the effluent was compliant mostly in winter time than summer time, and this observation was explained by the evaporation patterns that in summer when there is more solar radiation, the wastewater absorbed more heat and enhanced the evaporation rates which is directly related to both environmental and climatic parameters.

5.7 **References**

Adeniji, A. O., Okoh, O. O. and Okoh, A. I. (2017) 'Petroleum Hydrocarbon Fingerprints of Water and Sediment Samples of Buffalo River Estuary in the Eastern Cape Province , South Africa', *Journal of Analytical Methods in Chemistry*, pp. 1–13.

Alonso-Sáez, L., Gasol, J.M. Lefort, T. Hofer, J. and Sommaruga, R. (2006) 'Effect of natural sunlight on bacterial activity and differential sensitivity of natural bacterioplankton groups in Northwestern Mediterranean coastal waters', *Applied and Environmental Microbiology*, 72(9), pp. 5806–5813. doi: 10.1128/AEM.00597-06.

Aniyikaiye, T. E., Oluseyi,T. Odiyo, J.O and Edkpayi, J.N. (2019) 'Physico-Chemical Analysis of Wastewater Discharge from Selected Paint Industries in Lagos , Nigeria', *International Journal oF Environmental Research and Pu*, 16, pp. 1–17. doi: 10.3390/ijerph16071235.

Bennett, G. F. and Peters, R. W. (1988) 'The removal of oil from wastewater by air flotation: A review', *Critical Reviews in Environmental Control*, 18(3), pp. 189–253. doi: 10.1080/10643388809388348.

Bhateria, R. and Jain, D. (2016) 'Water quality assessment of lake water: a review'. *Springer International Publishing*, 2(2), pp. 161–173. doi: 10.1007/s40899-015-0014-7.

Changmai M, Pasawan M, Purkait MK (2017) 'Treatment of oily wastewater from drilling site using electrocoagulation followed by microfiltration'. *Seperation and Purification Technology* 210. pp, 463–472

Demicrci S., Erdogan B. and Oezcicmder R. (1998) 'Wastewater treatment at the petroleum refinery, Kirikale, Turkey using some coagulants and Turkish clays as coagulant aids', *Water Res.*, 32, pp. 3495-3499.

Dincer A.R., Karakaya N., Gunes E. and Gunes Y. (2008) ' Removal of COD from oil recovery industry wastewater by the Advanced Oxidation Processes (AOP) based on H2O2, Glob. N. J' 10, pp. 31-38.

Department of Water Affairs. (2013) *Revision of general authorisations in terms of Section 39 of*

the National Water Act, 1998 (Act No. 36 of 1998), No. 665. Government Gazette No. 36820, 6 September. Department of Water Affairs, Pretoria, South Africa.

Edokpayi, J. N., Odiyo, J. O. and Durowoju, O. S. (2017) *Impact of Wastewater on Surface Water quality in Developing Countries: A study of South Africa*, *Water Quality. Chapter 18. Intech*. doi: http://dx.doi.org/10.5772/57353.

Ehiagbonare, J. E. and Ogunrinde, Y. O. (2010) 'Physico-chemical analysis of fish pond water in Okada and its environs , Nigeria', *African Journal of Biotechnology*, 9(36), pp. 5922–5928.

Farajnezhad, H. and Gharbani, P. (2012) 'Coagulation Treatment of Wastewater in Petroleum Industry using Poly Aluminium Chloride and Ferric', *International Journal of Recent Research and Applied Studies*, 13(1), pp. 306–310.

Fatoki, O. S., Gogwana, P. and Ogunfowokan, A. O. (2003) 'Pollution assessment in the Keiskamma River and in the impoundment downstream', *Water SA*, 29(2), pp. 183–187. doi: 10.4314/wsa.v29i2.4854.

Finch, J W and Hall, R. L. (2001) *Estimation of Open Water Evaporation*.

Fingas, M. (2015) 'Oil and Petroleum Evaporation', in *Handbook of Oil Spill Science and Technology*, pp. 205–223. doi: 10.1002/9781118989982.ch7.

Government Gazette (1984) *Requirements for the Purification of Wastewater or Effluent. Gazette No 9225, Regulation No 991, 18 May*.

Hanafy, M. and Nabih, H. I. (2007) 'Treatment of oily wastewater using dissolved air flotation technique', *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, 29(2), pp. 143–159. doi: 10.1080/009083190948711.

Havard, D. (2013) *Oil and Gas Production Handbook - An introduction to oil and gas production, transport, refining and petrochemical industry*.

Herndl, G. J., Mi, G. and Frick, J. (1993) 'Major role of ultraviolet-B in controlling bacterioplankton growth in the surface layer of the ocean', *N*, 361(February), pp. 717–719.

Hoffman, M. T., Cramer, M.D. Gillson, L. and Wallace, M. (2011) *Pan evaporation and wind run decline in the Cape Floristic Region of South Africa (1974 – 2005): implications for*

vegetation responses to climate change. doi: 10.1007/s10584-011-0030-z.

Igbinosa, E. O. and Okoh, A. I. (2009) 'Impact of discharge wastewater effluents on the physico-chemical qualities of a receiving watershed in a typical rural community', *International Journal of Environmental Science and Technology*, 6(2), pp. 175–182.

Izady A., Abdalla, O., Sadeghi, M., Majidi, M,. Karimi, A., and Chen M., (2016). Novel Approach to Modeling Wastewater Evaporation Based on Dimensional Analysis, *Water Resources Management*. Water Resources Management, 30, pp. 2801–2814. doi: 10.1007/s11269-016-1324-8.

Jirka, A. M. and Carter, M. J. (1975) 'Micro Semi-Automated Analysis of Surface and Waste Waters for Chemical Oxygen Demand', *Analytical Chemistry*, 47(8), pp. 1397–1402. doi: 10.1021/ac60358a004.

Kaur, A., Vats,S. Rekhi, S. Bhadwaj, A. Goel, J. Tanwar, R.S. Gaur, K.K. (2010) 'Physico-chemical analysis of the industrial effluents and their impact on the soil microflora', in *Procedia Environmental Sciences*, 2, pp. 595–599. doi: 10.1016/j.proenv.2010.10.065.

Li, X., Cao, X. Wu, G. Temple, T. Coulon, F. and Sui, H. (2014) 'Ozonation of diesel-fuel contaminated sand and the implications for remediation end-points', *Chemosphere*. Elsevier Ltd, 109, pp. 71–76. doi: 10.1016/j.chemosphere.2014.03.005.

Padaki, M., Murali. R.S. Abdullah, M.S. Misdan, N. Moslehyani, A. Kassim, M.A Hilal, N and Ismail, A.F. (2015) 'Membrane technology enhancement in oil-water separation. A review', *Desalination*. Elsevier B.V., 357, pp. 197–207. doi: 10.1016/j.desal.2014.11.023.

Roderick, M.L. and Farquhar, G.D (2002) ' The cause of decreased pan evaporation over the past 50 years'.*Science*, 298, pp. 1410–1411.

Roderick, M.L, Rotstayn, L.D, Farquhar G.D, Hobbins, M.T. (2007) 'On the attribution of changing pan evaporation. *Geophys Res Lett*, 34, pp.251–270.

U.S. Department of Commerce (1970) Climatological Summary. Brownsville, Texas, pp. 46

Saber A., Hasheminejad H. Taebi A. and Ghaffari G. (2014) 'Optimization of Fenton-based treatment of petroleum refinery wastewater with scrap iron using response surface methodology'

Applied Water Science, 4, pp. 283-290.

Samudro, G. and Mangkoedihardjo, S. (2014) 'Review on BOD , COD and BOD / COD ratio : a triangle zone for toxic , biodegradable and stable levels', *International Journal Of Academic Research*, 2(4), pp. 235–239.

Sommaruga, R., Obernosterer, I. Herndl, G.J And Psenner, R. (1997) 'Inhibitory effect of solar radiation on thymidine and leucine incorporation by freshwater and marine bacterioplankton', *Applied and Environmental Microbiology*, 63(11), pp. 4178–4184. doi: 10.1128/aem.63.11.4178-4184.1997.

Sommaruga, R., Hofer, J.S. Alonso-Sa´ez, L and Gasol, J.M (2005) 'Differential sunlight sensitivity of picophytoplankton from surface Mediterranean coastal waters', *Applied and Environmental Microbiology*, 71(4), pp. 2154–2157. doi: 10.1128/AEM.71.4.2154-2157.2005.

Sonune, A. and Ghate, R. (2004) 'Developments in wastewater treatment methods', in *Desalination*, pp. 55–63.

Todd, G. D., Chessin, R. L. and Colman, J. (1999) Toxilogical Profile for Total Petroleum Hydrocarbons (TPH). *Public Health*.

Varjani S, Kumar G, Rene ER (2019) 'Treatment of wastewater from petroleum industry: current practices and perspectives', *Environmental Science and Pollution Research*, pp. 1–9. doi: 10.1007/s11356-019-04725-x.

Varjani, S. J. and Upasani, V. N. (2017) 'A new look on factors affecting microbial degradation of petroleum hydrocarbon pollutants', *International Biodeterioration and Biodegradation*. Elsevier Ltd, 120, pp. 71–83. doi: 10.1016/j.ibiod.2017.02.006.

Viggi, C. C. Presta, E. Bellagamba, M. Kaciulis, S. Balijepalli, S.K. Zanaroli, G. Papini, P.M. Rossetti, S. Aulenta, F. (2015) 'The BOil Spill Snorkel^: an innovative bioelectrochemical approach to accelerate hydrocarbons biodegradation in marine sediments' F*rontiers in Microbiology*. 6 (881), pp. 1–11. https://doi.org/10.3389/fmicb.2015.00881

Vuglinsky, V. S. (2009) 'Evaporation From Open Water Surface And Groundwater' *Hydrological Cycle*.

Webb, E. K. (1966) 'A pan-lake evaporation relationship', *Journal of Hydrology*, 4, pp. 1–11. doi: 10.1016/0022-1694(66)90063-1.

Whitman College (2015) 'Total Suspended Solids in Water Samples', Available at: https://www.whitman.edu/chemistry/edusolns_software/TSSBackground.pdf.

Wirnkor, V. A. Amonia, B. O. and Ngozi, V. E. (2014) 'Batch and Column Adsorption of BOD and COD in Vegetable Oil Industry Effluents Using Activated Carbon from Fluted Pumpkin (*Telfairia, Occidentalis.* Hook. F) Seed Shell', *International Letters of Chemistry, Physics and Astronomy*, 39, pp. 64–77. doi: 10.18052/www.scipress.com/ilcpa.39.64.

Winter, T.C. and Rosenberry, D.O. (1995) 'Evaluation of 11 equations for determining evaporation for a small lake in the north central United States' *Water Resource Research*, 31(4), pp. 983-993.

Xu, X. and Zhu, X. (2004) 'Treatment of refectory oily wastewater by electro-coagulation process', *Chemosphere*, 56, pp. 889–894. doi: 10.1016/j.chemosphere.2004.05.003.

Zenga ,Y., Yang C. Zhang J. and Pu W. (2007) ' Feasibility investigation of oily wastewater treatment by combination of zinc and PAM in coagulation/flocculation, *Journal of Hazardous Materials*' 147, pp. 991-96.

CHAPTER 6 : DEVELOPMENT OF THE OIL PRODUCED WATER MODEL TO BE USED FOR ASCERTAINING THE COMPLIANCE TO GUIDELINES

The chapter focuses on the development and implementation of a model to be as an indicator of a pollution caused by the oil produced water and be used as a predictive tool for cases of non-compliance. The results obtained in the previous chapter (chapter 5) were applied to develop a multiplicative model. The details on the development of the model using the rate of evaporations patterns will be discussed in detail.

6.1 **Introduction**

With the advancement of technology and industrial growth, the contamination of freshwater resources has become a global issue. The world is observing an increase in urbanization and industrialization due to the consumerist approach (Li and Yu, 2011; Zhang *et al.*, 2015). Water quantity is as important as water quality and therefore both aspects need to be given the due weight. This means that the strategies of minimizing industrial waste need to be implemented. Managing environmental pollution is a legal requirement, and one of the ways of managing it is to ensure the wastewater discharged from industries do not cause harmful damages to the environment. Normally, laboratory testing of collected samples is one way to ensure that the chemical composition of the effluent meet the stipulated discharge limits enforced by the regulators. However, this might be a challenge for many oilfields because it is time consuming, expensive (since many oilfields do not have laboratories with relevant equipment to analyze the effluents), and moreover some testing techniques and approaches may even lead to secondary pollution because some tests involve the use of toxic chemicals and reagents. Therefore, this study explored the possibility of developing a model using dimensional analysis to predict the compliance of the effluent.

Oil produced water evaporation (OPWE) is highly nonlinear in nature, thus prompting the search for models that are capable of addressing this tendency of non-linearity's in the process since it cannot be directly ascertained but only estimated depending on either the energy or water budget

or mass transfer approaches (Sudheer *et al.*, 2002). Thus, dimensional analysis based on Buckingham π theorem was employed for this study.

6.2 **Model development based on Buckingham pi theorem.**

A model is a simplification of the reality on the ground. In general, it is a representation between the source and a target (Sibel, 1998; Boulter and Gilbert, 1996), the target being an unknown phenomenon or object needs to be explained, and the source being a familiar phenomenon or object assisting the scientists to understand the target. Models play central roles in expert scientists' reasoning and problem-solving (Clement, 1989); Chi, Feltovich and Glaser, 1981; Larkin, 1981; Reif, 1983) and they are instrumental in summarizing data, making predictions, justifying outcomes and facilitating communication in science. To the best of our knowledge, there's no model developed to predict compliance of the wastewater effluent and dimensional analysis based on Buckingham pi theorem (Buckingham, 1914) was to be used to formulate a multiplicative equation (equation 6.1).

$$OPWE = \frac{C\,R}{W^2\,TDS}\left(\frac{W^2\,TDS\,CWE}{R}\right)^{\alpha}\left(\frac{R\,EC}{W^3\,TDS}\right)^{\beta}\left(\frac{TPH}{TDS}\right)^{\gamma}\left(\frac{TSS}{TDS}\right)^{\delta}\left(\frac{TOC}{TDS}\right)^{\varepsilon}\left(\frac{BOD}{TDS}\right)^{\mu}\left(\frac{COD}{TDS}\right)^{\rho}\left(\frac{T_{OPW}}{T_a}\right)^{\omega} \quad (6.1)$$

The details of the steps for the model development have been given in Chapter 3 in section 3.8 of this dissertation

6.2.1 **Obtaining the coefficients**

The data collected from the oil field (May - December 2019) was randomized to minimize bias and the coefficients were determined by regression analysis using a software known as statistical package for the social sciences (SPSS). 70% of the data was used for calibration the coefficients were obtained (C, α, β, γ, δ, ε, μ, ρ and ω.) and the remaining 30% was used for validation. The reason to subdivide the data into two is because, the calibration curve is to train the data set and the validation is for estimate prediction error in order to compare models. The data was fitted to a nonlinear regression analysis since OPWE is nonlinear in nature. The general equation was entered as the theoretical expression is SPSS. To determine the coefficients, SPPS was provided with the starting value for each constant and it was then used an iterative method to change the

values of the constants to get the best fit of nonlinear expression that fits the data. Therefore, the SPSS gave an iteration history with an iterative table indicating how many steps the iteration takes from the starting value to the end to get the best fit results.

6.2.2 **Statistical analysis**

Based on the regression analysis form the statistical package for social sciences (IBM SPSS Statistics 22), the constants of Eq. (6.1) were obtained as C=200.337, α=0.8028, β=−0.0487, γ=-0.191, δ =1.130 , ε =0.0326 , μ= 0.707 , ρ = -1.1690 and ω = 0.157 leading to the final mathematical model (equation 6.2) as follows:

$$(\mathrm{OPWE}) = \frac{200.34R}{W^2.TDS}\left(\frac{W^2.TDS.CWE}{R}\right)^{0.80}\left(\frac{R.EC}{W^3.TDS}\right)^{-0.05}\left(\frac{TPH}{TDS}\right)^{-0.19}\left(\frac{TSS}{TDS}\right)^{1.13}\left(\frac{TOC}{TDS}\right)^{0.03}\left(\frac{BOD}{TDS}\right)^{0.71}\left(\frac{COD}{TDS}\right)^{-1.17}\left(\frac{T_{OPW}}{T_a}\right)^{-0.16} \quad (6.2)$$

Where:

OPWE is oil produced water evaporation

CWE is the clear evaporation

TDS is the total dissolved solids

TSS is the total suspended solids

EC is the electrical conductivity

Ta is the air temperature

R is the solar radiation

W is the wind speed

Topw is the oil produced water temperature

TPH is total petroleum hydrocarbon

COD is chemical oxygen demand

BOD is biological oxygen demand

TOC is the total organic carbon

6.2.3 **Estimation of OPWE using dimensional analysis results**

From the calibration data set, the estimated OPWE was obtained by fitting the coefficients values to equation (6.2) and statistical chemometrics used to characterize the external predictivity of a model were coefficient of determination (R^2), and relative mean absolute error (RMSE) in order to evaluate the effectiveness and the accuracy of the proposed method. These chemometrics were calculated using OPWE measured and OPWE estimated. The data was randomized until the best randomized set of data was obtained with high R^2 and low RMSE. From the validation data set the OPWE estimated was calculated and the chemometrics methods were also be calculated using OPWE measured and OPWE estimated (Table: 6.1).

Table 6.1: **Statistical chemometrics of the proposed method**

Phase	R^2	RMSE (mm/day)	MAE
calibration	0.70	0.49	0.33
validation	0.73	0.47	0.35

6.2.4 **(Coefficient of determination R^2)**

R^2 is generally defined as the square of the correlation coefficient between observed and predicted values in a regression (Alexander, Tropsha and Winkler, 2015). The aim of the coefficient of determination analysis was to determine how well the model fits the data. As Table 6.1 showed, the regression model for calibration accounted for 70% of the variance which can be explained by the entire data set of dependent variables while for validation purpose it accounted for 73%. This suggest that the more variance that is accounted for by the regression model the closer the data points will fall to the fitted regression line. Moreover, derived equation fairly predicts the oil produced evaporation. The R^2 obtained in this study is similar to the one reported for modelling wastewater evaporation using dimensional analysis in Oman ((Izady *et al.*, 2016).

6.2.5 **Relative mean absolute error and (RMSE) and mean absolute error (MAE)**

RMSE is a common metric that is normally used to measure the accuracy for continuous variables and for this reason it was employed in model evaluation in this study. It is defined as a quadratic scoring rule that also measures the average magnitude of the error. It's the square root of the average of squared differences between prediction and actual observation (equation 6.3). This metric has been used in many fields including in meteorology, air quality, and climate research studies (Chai and Draxler, 2014). As shown in Table 6.1, the RMSE statistic, which is a measure of the global goodness of fit between the estimated and measured OPWE evaporation is 0.43 mm which is satisfactory because lower values indicate better fit. Another useful metric was used for model evaluations which is known as the mean absolute error (MAE) (equation 6.3). which is used to quantify the prediction accuracy of the proposed method is 0.33 %.

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{j=1}^{n}(y_j - \hat{y}_i)} \qquad \mathrm{MAE} = \frac{\sum_{j=1}^{n} \mathrm{abs}(y_{j-} \lambda(x_j))}{n} \quad (6.3)$$

6.3 **Model application for real environment simulation**

Data that was obtained during the oil refinery experiments were applied on the multiplicative developed model to generate an output file (predicted value). The output data from the model was compared to estimated obtained from the developed model. The words prediction" and "estimation" are sometimes used interchangeably in non-technical writing and they seem to function similarly however, in a statistical problem, particularly for modelling, there's a sharp difference between them. It is imperative to note the difference because an estimator uses data to guess at a parameter while a predictor uses the data to guess at some random value that is not part of the dataset. Therefore, the developed model has the potential to be used to predict the compliance of the effluents from oil refinery industries.

Therefore, the evaluated equation 6.2 was reduced to a simple linear relationship:

From equation 6.2; let $\frac{W^2\ TDS}{R} = K$

Leading to equation 6.3:

$$(K.OPWE) = C(K.CWE)^{0.80}\left(\frac{EC}{K.W}\right)^{-0.05}\left(\frac{TPH}{TDS}\right)^{-0.19}\left(\frac{TSS}{TDS}\right)^{1.13}\left(\frac{TOC}{TDS}\right)^{0.03}\left(\frac{BOD}{TDS}\right)^{0.71}\left(\frac{COD}{TDS}\right)^{-1.17}\left(\frac{T_{OPW}}{T_a}\right)^{-0.16} \quad (6.3)$$

Let $K.OPWE = Y$ and applying the natural logarithm this will lead to the linear equation:

$$LnY = Ln(200.34) + 0.80Ln(K.CWE) - 0.05\,Ln\left(\frac{EC}{K.W}\right) - 0.19Ln\left(\frac{TPH}{TDS}\right) + 1.13Ln\left(\frac{TSS}{TDS}\right) + 0.03Ln\left(\frac{TOC}{TDS}\right) + 0.71Ln\left(\frac{BOD}{TDS}\right) - 1.17Ln\left(\frac{COD}{TDS}\right) - 0.16Ln\left(\frac{T_{OPW}}{T_a}\right) \quad (6.4)$$

Fitting the coefficients obtained from data set lead to the final linear equation:

$Y = 5.30 + 0.8028X_1 - 0.0487X_2 - 0.191X_3 + 1.13X_4 + 0.03X_5 + 0.71X_6 - 1.17X_7 - 0.16X_8$ ..... (6.5)

Where x_1 to x_8 are dependent parameters.

6.4 **Conclusion**

Statistical prediction models inform decision-making processes in many real-world settings. Before putting these predictions into practice, one must extremely thoroughly and carefully test and validate candidate models to ensure that the proposed predictions have enough accuracy to be used in practice. In this study, a multiplicative model was developed to predict compliance of the OPW using dimensional analysis. The study saw it fit to develop this model since industries dealing with activities that lead to discharge of OPW, for instance petrochemical plants and petroleum refineries are facing problem of disposing the waste generated (both solid/water). Issues related to wastewater from petroleum industries contains different types of organic and inorganic pollutants such as, sulfides, BTEX (benzene, toluene, ethylbenzene and xylene), hydrocarbons, phenol, and heavy metals (He and Jiang 2008; Usman et al. 2012; Varjani 2017a; Raza et al.2018). The reason arising from these industries that face challenges in disposing the wastewater include the effectiveness of the various treatment used to treat the water and appropriately checking the compliance of the wastewater prior to being discharged into the environment. OPW industries are among the fastest growing industries which implies that large quantities of toxic wastewater have to be released to the environment. This implies that there's a huge amount wastewater that need to be verified for compliance. Moreover, other test such COD

analysis are known to involve the use of hazardous chemicals and reagents such as hexavalent chromium, sulfuric acid, mercury, and other hazardous substances depending on the method used (Dubber and Gray, 2010). All this is associated with the possibility that may lead to secondary pollution therefore, the developed model can eliminate such mishaps and can also save time and costs for the industries. OPWE from different processes may have similar chemical composition but in different levels and ratios. This can be exploited to differentiate them using the same developed model as the coefficients pattern will be characteristic to a certain OPW. The model can then be used to fingerprint and identify culprits in case of discrepancies.

6.5 **Reference**

Alexander, D. L. J., Tropsha, A. and Winkler, D. (2015) 'Beware of R2 : simple, unambiguous assessment of the prediction accuracy of QSAR and QSPR models', *Journal of Chemical Information and Modeling*, 55(7), pp. 1–16. doi: 10.1016/j.physbeh.2017.03.040.

Buckingham, E. (1914) 'On physically similar systems; Illustrations of the use of dimensional equations', *Physical Review*, 4(4), pp. 345–376. doi: 10.1103/PhysRev.4.345.

Chai, T. and Draxler, R. R. (2014) 'Root mean square error (RMSE) or mean absolute error (MAE)? -Arguments against avoiding RMSE in the literature', *Geoscientific Model Development*, 7(3), pp. 1247–1250. doi: 10.5194/gmd-7-1247-2014.

Chi, M. T. H., Feltovich, P. J. and Glaser, R. (1981) 'Categorization and representation of physics problems by experts and novices', *Cognitive Science*, 5(2), pp. 121–152. doi: 10.1207/s15516709cog0502_2.

Clement, J. (1989) 'Learning via Model Construction and Criticism', in *Handbook of Creativity*, pp. 341–381. doi: 10.1007/978-1-4757-5356-1_20.

Dubber, D. and Gray, N. F. (2010) 'Replacement of chemical oxygen demand (COD) with total organic carbon (TOC) for monitoring wastewater treatment performance to minimize disposal of toxic analytical waste', *Journal of Environmental Science and Health - Part A*, 45(12), pp. 1595–1600. doi: 10.1080/10934529.2010.506116.

Izady, A., Abdalla, O. Sadeghi, M. Majidi, M. Karimi, A. and Chen . (2016) 'A Novel Approach to Modeling Wastewater Evaporation Based on Dimensional Analysis', *Water Resources Management*. Water Resources Management, 30(8), pp. 2801–2814. doi: 10.1007/s11269-016-1324-8.

Larkin, J. H. (1981) 'Enriching formal knowledge: A model for learning to solve textbook physics problems', in *Cognitive skills and their acquisition*, pp. 311–334.

Li, W. W. and Yu, H. Q. (2011) 'From wastewater to bioenergy and biochemicals via two-stage bioconversion processes: A future paradigm', *Biotechnology Advances*. Elsevier Inc., 29(6), pp. 972–982. doi: 10.1016/j.biotechadv.2011.08.012.

Reif, F. (1983) 'How can chemists teach problem solving? Suggestions derived from studies of cognitive processes', *Journal of Chemical Education*, pp. 948–953. doi: 10.1021/ed060p948.

Sibel, E. (1998) *Modeling in Chemistry as Cuktural Practice: A Theoretical Framework with Implications for Chemistry Education*.

Sudheer, K. P., Gosain, A.K. Mohana R.D. and Saheb, S.M. (2002) 'Modelling evaporation using an artificial neural network', *Hydrological Processes*, 16, pp. 3189–3202.

Varjani, S. J. and Upasani, V. N. (2017) 'A new look on factors affecting microbial degradation of petroleum hydrocarbon pollutants', *International Biodeterioration and Biodegradation*. Elsevier Ltd, 120, pp. 71–83. doi: 10.1016/j.ibiod.2017.02.006.

Zhang, X., He, W. Ren, L. Stager, J. Evans, P. and Logan, B.E. (2015) 'COD removal characteristics in air-cathode microbial fuel cells', *Bioresource Technology*. Elsevier Ltd, 176, pp. 23–31. doi: 10.1016/j.biortech.2014.11.001.

CHAPTER 7 : CONCLUSION AND FUTURE RECOMENDATIONS

7.1 **General conclusion**

The work reported in this dissertation has shown that, oil produced water emanating from oil companies such as oil processing companies, refinery and petroleum industries contain many chemicals that are potentially hazardous to the environment as well as to living organisms including human being. This work explored the characteristics of such wastewaters to reveal many of its characteristics which have shown that compliance by companies and industries in the oil sector is an issue. This work has worked on the development of a unique model that can be used to ascertain compliance of the discharged effluents which happen to enter either municipal channels or other water bodies such as rivers. This may lead to serious contamination of freshwater resources and therefore, this work has come up with a model that can be used by such industries as well as authorities tasked to enforce guidelines and regulations to limit the discharge of oily wastewaters.

In chapter 4 an analytical method based on gas chromatography coupled to time of flight-mass spectrometry (GC-TOF-MS) was developed for the determination of total petroleum hydrocarbons (TPHs) in oil produced water (OPW) from the petroleum industry. The effect of the organic solvent was studied, and n-hexane was found to be the best extraction solvent compared to other solvents by 96.28% extraction efficiency. The TPHs were determined in both influent and effluent samples. Various fractions were analyzed including, n-alkanes, branched alkanes, alkenes, etc. by gas chromatography analysis GC-TOF-MS. The winter period (June-August) registered many compounds especially from the influent compartments than they were found in autumn season. This suggests that the physical treatment does remove the TPHs however, it is suggested that the effluents should be subjected to secondary treatment since the primary treatment couldn't reduce the contamination level and make it in allowed limit for discharge into water bodies.

In Chapter 5 physico-chemical analyses of the OPW effluents were studied for regulatory purposes. The parameters investigated were within the acceptable threshold limits except for COD, TPH and EC that slightly surpassed. It is suggested that wastewater from the oil depot

should undergo secondary and/or tertiary treatment processes before discharging into the receiving bodies. The compliance study was imperative to be studied to evaluate if it can be predicted using the evaporation patters and it was found that it was possible. The elevated evaporation patterns were mostly observed in summer as is the period of warmer temperatures and high wind speeds that enhances the rates of evaporation.

In Chapter 6 the modelling approach based on experimental data collected was developed. A multiplicative model was developed to predict compliance of the OPW using dimensional analysis. The project saw fit since there's exponential economic development, and industrial growth, whereby there is demand for oil worldwide. The challenge many industries face include disposal of the generated oily wastewater because it has to comply with regulatory standards. To check compliance for many industries especially oil depot remains a challenge because of the facilities needed to ensure the chemical composition of the effluent is properly checked and it's within the stipulated criteria. As a result, a multiplicative model formulated, OPWE as a function of influencing parameters indicated a reasonably well accuracy (RMSE = 0.49) for the OPWE estimation. Furthermore, the model it's able to fingerprint since OPWE from different processes may similar chemical composition but in different levels and ratios. This can be exploited to differentiate them using the same developed model as the coefficients pattern will be characteristic to a certain OPWE.

The success in the development of a model to predict the compliance of the OPW is very significant from the economic point of view as it will enable industries that discharge oily wastewater to have a reliable means of monitoring their effluent. All companies and even other economic sectors are currently working on alternatives that can cut operation costs without compromising productivity and quality. For oil refinery industries, oil exploration and others can consider the approach developed in this work and possibly improve it, diversify in order to ensure accuracy, precision and reliability of the model.

Apart from these companies, municipals and other governmental or private entities which regulate OPW discharges can still adopt this concept to monitor and fingerprint effluents from companies' channels before they enter municipal or common collecting portals. This will imply that municipals will have the means to track culprits where there is poisoning of wastewater treatment plants

7.2 **Recommendations for Future Research**

The results from this work suggest that a simple and a reliable tool which is dimensional analysis based on Buckingham pi theorem can be used to develop a model to predict compliance of oily wastewater effluents from petroleum industries by making use of evaporation patterns. The findings in this study suggests a green, efficient, and cost-effective approach of checking compliance of oily wastewater samples which is very useful in eliminating a possibility of introducing a secondary pollution since most chemicals used to check compliance are toxic. However, further investigations are needed to be addressed before this model can be utilized by other companies and entities other than petroleum industries.

In this research, a surrogate standard, 1-chlorooctadecane was dissolved in ethyl acetate and the samples were extracted with DCM, ethyl acetate and n-hexane organic solvents whereby n-hexane gave a high extraction efficiency of 96%. Therefore, it would be interesting to examine the extraction efficiency of DCM, ethyl acetate and n-hexane organic solvents when the surrogate standard is dissolved in n-hexane. Further studies should focus on using other standards for quantitative analysis of TPHs rather than only focusing on the qualitative analysis.

One of the most important results from this project was a significant influence of the climatic and environmental parameters on the rate of the evaporation in order to evaluate if the evaporation patterns can be used to predict the oily wastewater compliance. The compliance study did prove that it is possible to use the evaporation patterns. However, after the successful development of a model, future work may need to refine, improve this model, and use it as a baseline platform to establish similar models in other types of oily wastewaters from other similar industries. This will generate appropriate models that can be suitable for checking compliances in all wastewaters from oil companies.

APPENDICES

APPENDIX 1

Rate possibilities

1. TPH and R were taken as repeating parameters

$\pi_1 = \boldsymbol{TPH} * \boldsymbol{R} * OWE$

$(LMT)^0 = (ML^{-3})^{a_1}(MT^{-3})^{b_1} LT^{-1}$

$L^0 M^0 T^0 = M^a L^{-3a_1} M^b T^{-3b_1} L^1 T^{-1}$

L: $-3a_1 + 1$ …… (1)

$3a_1 = -1$

$\therefore a = -\frac{1}{3}$

$M: a_1 + b_1$ …… (2)

$b_1 = -a_1$

$T: -3b_1 - 1$ …… (3)

$3b_1 = 1$

$\therefore b = \frac{1}{3}$

$\pi_1 = TPH^{-1/3} * R^{1/3} * OWE$

Not dimensionless therefore, incorrect possibility.

Accumulation possibilities

2. TPH and R were taken as repeating parameters

$\pi_1 = \boldsymbol{TPH} * \boldsymbol{R} * OWE$

$(LMT)^0 = (ML^{-3})^{a_1}(MT^{-2})^{b_1}L$

$L^0M^0T^0 = M^aL^{-3a_1}M^bT^{-2b_1}L^1$

L: $-3a_1 + 1$ …… (1)

$3a_1 = -1$

$\therefore a = -\frac{1}{3}$

$M: a_1 + b_1$ …… (2)

Substitute a value into equation 2

$b_1 = -a_1$

$\therefore b = \frac{1}{3}$

$T: -2b_1$ …… (3)

$\pi_1 = TPH^{-1/3} * R^{1/3} * OWE$

Not dimensionless therefore, incorrect possibility

3. TSS, W and EC were taken as repeating parameters

$\pi_1 = \boldsymbol{TSS} * \boldsymbol{W} * \boldsymbol{EC} * OWE$

$(L\ M\ T)^0 = (M\ L^{-3})^a\ (L\ T^{-1})^b\ (T^{-1})^c\ L$

$L^0 M^0 T^0 = M^a L^{-3a}\ L^b T^{-b} T^{-c}\ L^1$

L: -3a + b + 1 …… (1)

M: a + 0 ∴a = 0 …… (2)

T: -b -c ∴ b = -c ……...…… (3)

Substituting equation 2 into equation 1

-3(0) + b + 1 = 0

b = -1

Substituting b value into equation 3

-c = -1

c = 1

$\therefore\ \pi_1 = TSS^0 * W^{-1} * EC^1 * OWE$

$\pi_1 \therefore \frac{EC * OWE}{W}$

$\pi_2 = \boldsymbol{TSS} * \boldsymbol{W} * \boldsymbol{EC} * CWE$

$(L\ M\ T)^0 = (M\ L^{-3})^{a2}\ (L\ T^{-1})^{b2}\ (T^{-1})^{c2}\ L$

$L^0 M^0 T^0 = M^a L^{-3a2}\ L^{b2} T^{-b2} T^{-c2}\ L^1$

L: $-3a_2 + b_2 + 1$ …….. (1)

M: $a_2 + 0$ $\therefore a = 0$ …… (2)

T: $-b_2 - c_2$ $\therefore b = -c_2$ ……..…… (3)

Substituting equation 2 into equation 1

$-3(0) + b_2 + 1 = 0$

$b_2 = -1$

Substituting b value into equation 3

$-c_2 = -1$

$c_2 = 1$

$\therefore\ \pi_2 = TSS^0 * W^{-1} * EC^1 * CWE$

$\pi_2 \therefore \frac{EC * CWE}{W}$

$\pi_3 = \boldsymbol{TSS} * \boldsymbol{W} * \boldsymbol{EC} * R$

$$(L\ M\ T)^0 = (M\ L^{-3})^{a3}\ (L\ T^{-1})^{b3}\ (T^{-1})^{c3}\ MT^{-2}$$

$$L^0 M^0 T^0 = M^{a3} L^{-3a3}\ L^{b3} T^{-b3}\ T^{-c3} M^1 T^{-2}$$

$$L: -3_{a3} + b \ \ldots\ldots\ldots\

4. **W, R and TSS** were chosen as the repeating parameters:

$$\pi_1 = \boldsymbol{W}.* \boldsymbol{R} * \boldsymbol{TPH} * OWE$$

$$(LMT)^0 = (LT^{-1})^a (MT^{-2})^b (ML^{-3})^c L$$

$$L^0 M^0 T^0 = L^a T^{-a} M^b T^{-2b} M^c L^{-3c} L^1$$

L: a – 3c + 1 …….. (1)

M: b + c b = - c …….. (2)

T: -a – 2b a = -2b …….. (3)

Substitute equations 2 and 3 into equation 1

$$\therefore -2b - 3(-b) + 1 = 0$$

$$-2b + 3b + 1 = 0$$

b = -1

Substitute b value into equation 3.

a = -2(-1) = 2

$$\therefore \pi_1 = W^2 * R^{-1} * THP * OWE$$

$$\pi_2 = \boldsymbol{W}.* \boldsymbol{R} * \boldsymbol{TPH} * OWE$$

$$(\mathrm{LMT})^0 = (\mathrm{LT}^{-1})^{a2}(\mathrm{MT}^{-2})^{b2}(\mathrm{ML}^{-3})^{c2}\mathrm{L}$$

$$(\mathrm{L}^0\mathrm{M}^0\mathrm{T}^0) = \mathrm{L}^{a2}\mathrm{T}^{-a2}.\mathrm{M}^b\mathrm{T}^{-2b2}.\mathrm{M}^{c2}\mathrm{M}^{-3c2}\mathrm{L}^1$$

L: a_2 -3c_2 + 1 …….. (1)

M: b_2 + c_2 …….. (2)

T: $-a_2 - 2b_2$ …… (3)

Substitute Equation 2 into equation 1

∴ $-2b_2 - 3(-b_2) + 1 = 0$

$-2b_2 + 3b_2 + 1 = 0$

$b_2 = -1$

Substitute b_2 value into equation 1

$C_2 = 1$

Substitute b value into equation 1

$a_2 = -2(-1)$

$a_2 = 2$

Substitute b value into equation 3.

a = -2(-1) = 2

$$\pi_2 = W^2 * R^{-1} * THP * CWE$$

$$\pi_3 = \boldsymbol{W}.* \boldsymbol{R} * \boldsymbol{TPH} * EC$$

$$(LMT)^0 = (LT^{-1})^{a_3}(MT^{-2})^{b_3}(ML^{-3})^{c_3}T^{-1}$$

$$(L^0M^0T^0) = L^{a_3}T^{-a_3}M^{b_3}T^{-2b_3}M^{c_3}L^{-3c_3}T^{-1}$$

L: $a_3 - 3c_3$ ∴$a_3 = 3c_3$ …… (1)

M: $b_3 + c_3$ ∴$b_3 = -c_3$…… (2)

T: $-a_3 - 2b_3 - 1$ …… (3)

Substitute equation 1 and 2 into equation 3

$-(3c_3) - 2(-c_3) - 1 = 0$

$-3c_3 + 2c_3 - 1 = 0$

$-c_3 - 1 = 0 \quad \therefore c_3 = -1$

Substitute c value into equation 2……. ALSO …substitute c into equation 1

$b_3 + c_3 = 0$ $\qquad$ $a_3 - 3c_3 = 0$

$\therefore a_3 = 3c_3$

$b_3 - 1 = 0$ $\qquad$ $a_3 = 3(-1)$

$b_3 = 1$ $\qquad$ $a_3 = -3$

$\therefore \pi_3 = W^{-3}.R.\ TPH^{-1}.EC$

$\pi_4 = \boldsymbol{W} * \boldsymbol{R} * \boldsymbol{TPH} * TSS$

$(LMT)^0 = (LT^{-1})^{a_4}(MT^{-2})^{b_4}(ML^{-3})^{c_4}ML^{-3}$

$L^0M^0T^0 = L^{a_4}T^{-a_4}M^{b_4}T^{-2b_4}M^{c_4}L^{-3c_4}M^1L^{-3}$

L: $a_4 - 3c_4 - 3$ …… (1)

M: $b_4 + c_4 + 1$ $\qquad$ $c_4 = -b_4 - 1$ …… (2)

T: $-a - 2b$ $\qquad$ $a_4 = -2b_4$ …… (3)

Substitute equations 2 and 3 into equation 1

$-2b_4 - 3(-b_4 - 1) - 3 = 0$

$-2b_4 + 3b_4 + 3 - 3 = 0$

$b_4 = 0$

Substitute b value into equation 3

$-a_4 = -2b_4$

$a_4 = 0$

Substitute b value into equation 2

$c_4 = -b_4 - 1$

$c_4 = 0 - 1$

$c = -1$

$\pi_4 = W^0 . R^0 . TPH^{-1} . TSS$

$\therefore \pi_4 = \frac{TSS}{TPH}$

$\pi_5 = \boldsymbol{W} * \boldsymbol{R} * \boldsymbol{TPH} * COD$

$(LMT)^0 = (LT^{-1})^{a_5} (MT^{-2})^{b_5} (ML^{-3})^{c_5} ML^{-3}$

$L^0 M^0 T^0 = L^{a_5} T^{-a_5} M^{b_5} T^{-2b_5} M^{c_5} L^{-3_5} ML^{-3}$

L: $a_5 - 3c_5 - 3$ …… (1)

M: $b_5 + c_5 + 1$; $c = -b_5 - 1$ …….…….. (2)

T: $-a_5 - 2b_5$; $a = -2b_5$ ……..…… (3)

Substitute equations 2 and 3 into equation 1

$-2b_5 - 3(-b_5 - 1) - 3 = 0$

$-2b_5 + 3b_5 + 3 - 3 = 0$

$b_5 = 0$

Substitute b value into equation 3

a= = -2b

$a_5 = 0$

Substitute b value into equation 2

$c_5 = -b - 1$

$c_5 = 0 - 1$

$c_5 = -1$

$\pi_5 = W^0 . R^0 . THP^{-1} . COD$

$\pi_5 = \frac{COD}{TPH}$

$\pi_6 = \frac{T_w}{T_a}$

$\pi_7 = \frac{BOD}{COD}$

$\pi_8 = \frac{BOD}{TOC}$

$\pi_9 = \frac{TDS}{TSS}$

After solving the pi terms. A general formula will be obtained:

$\pi_1 = f\left(\pi_2, \pi_3, \pi_4\, \pi_5, \pi_6, \pi_7, \pi_8, \pi_9,\right)$

Following dimensional analysis based on Buckingham pi theorem:

$$OWE = \frac{R}{W^2TPH} f\left(\frac{W^2TPHCWE}{R}, \frac{REC}{W^3TPH}, \frac{TSS}{TPH}, \frac{COD}{TPH}, \frac{T_w}{T_a}, \frac{BOD}{COD}, \frac{BOD}{TOC}, \frac{TDS}{TSS}\right)$$

Incorrect possibility, according to Buckingham π theorem each parameter should be used once.

Appendix: 1